

NEW ELECTRON TRANSFER PATHWAYS IN THE
REACTIONS OF ORGANIC ONIUM SALTS
AND ORGANOMERCURIC HALIDES

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

By
RAJIVE KUMAR KHANNA

TH
CHM/1982/D
W42

to the

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
DECEMBER, 1982

Dedicated

to

my parents

who are my source of strength
and inspiration.

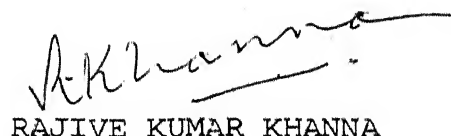
*What we know here is very little,
but what we are ignorant of is
immense.*

- LAPLACE

STATEMENT

I hereby declare that the matter embodied in this thesis, "NEW ELECTRON TRANSFER PATHWAYS IN THE REACTIONS OF ORGANIC ONIUM SALTS AND ORGANOMERCURIC HALIDES" is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor P.R. Singh.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.



RAJIVE KUMAR KHANNA

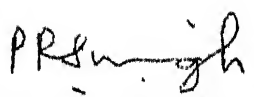
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CERTIFICATE

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(P. R. SINGH)
Professor of Chemistry
Thesis Supervisor

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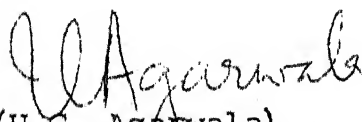
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CERTIFICATE OF COURSE WORK

This is to certify that Mr. Rajive Kumar Khanna has satisfactorily completed all the course requirements for the Ph.D. degree programme in Chemistry. The courses include:

Chm 500 Mathematics for Chemists I
Chm 501 Advanced Organic Chemistry I
Chm 521 Chemical Binding
Chm 523 Chemical Thermodynamics
Chm 541 Advanced Inorganic Chemistry I
Chm 800 General Seminar
Chm 801 Students Seminar
Chm 900 Research

Mr. Rajive Kumar Khanna has successfully completed his Ph.D. qualifying examinations in October 1977.


(U.C. Agarwala)
Professor and Head
Department of Chemistry,
IIT-Kanpur


(S. Chandrasekaran)
Convener,
Departmental Post-
Graduate Committee,
Dept. of Chemistry,
IIT- KANPUR

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It is with great pleasure and pride that I avail of this opportunity to express my deep sense of gratitude to my thesis supervisor Professor P.R. Singh, for suggesting the research problems and providing me with zeal and enthusiasm by his inspiring guidance and constructive criticism, with perfect understanding and endurance, throughout the period of my stay at I.I.T., Kanpur.

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A special word of appreciation is due to Mr. R.D. Singh for his elegant typing of the thesis, Mr. B.N. Shukla and Ram Singh Chauhan for cyclostyling. Cooperation and services received from the staff of the central facilities, departmental office, stores and workshops are sincerely appreciated with a special acknowledgement of the help from Mr. Kailash Arora, Mr. Anirudh Raut and Mr. L.P. Tripathi.

I am deeply beholden to the members of my family: my brothers, my sister-in-law, my sister and my aunt for their abiding inspiration and loving patronage.

My thanks are due to the authorities of the Indian Institute of Technology, Kanpur and the Council of Scientific and Industrial Research, New Delhi for financial support.

Last, but definitely not the least, I wish to express my deep appreciation for my wife, Bhawna, for her immense patience and understanding. Her cooperation, by not bothering me ever with the mundane household problems, is gratefully acknowledged.

RAJIVE KUMAR KHANNA

PREFACE

In recent years, the chemistry of organic electron transfer reactions and radical anion intermediates in various organic and organometallic transformations has gained immense significance. Many reactions which formally appeared in the earlier literature to proceed by ionic or unknown pathways have been conclusively proved to involve electron transfer free radical mechanisms. Reports during the past few years, particularly from the laboratories of Professors, G.A. Russell, N. Kornblum, J.F. Bunnett, E.C. Ashby, R.K. Norris, G.D. Sargent, S. Bank, J.F. Garst, J.K. Kochi, R.A. Rossi and W.A. Pryor have added newer dimensions to the fast developing field of electron transfer reactions. Radical anion intermediates produced as a consequence of electron transfer or coupling between radicals and anions are now found to intervene in a large variety of organic and organometallic reactions. A new mechanistic class of reactions symbolized by $S_{RN}1$ has emerged.

This thesis entitled, "New Electron Transfer Pathways in the Reactions of Organic Onium salts and Organomercuric Halides" presents novel mechanistic findings and describes several important aspects of electron transfer mechanisms of reactions broadly classified under four categories, namely (i) the reactions of diaryliodonium cations with ambident 2-nitropropanate anion, (ii) autoinitiated and induced dediazoniations with ambident nitrite and 2-nitropropanate anions, (iii) the reactions of arene-diazonium cations with Grignard reagents, and (iv) reductive

demercuration and symmetrization of organomercuric halides by sodium naphthalene and lithium aluminium hydride. The subject matter of this thesis has been divided into six chapters. The first chapter deals with a general review on "Electron Transfer Reactions and Radical Anion Intermediates," based on the existing literature. Each of the Chapters II through V has been further subdivided into (1) Abstract, (2) Introduction, (3) Results and Discussion, (4) Experimental, and (5) References. Introduction to each chapter covers a brief literature survey pertinent to the topic under consideration. Sequential numbering of schemes, equations, tables, figures, structures, and references has been repeated for every chapter.

Chapter II presents mechanistic studies on the reactions of diphenyliodonium bromide, phenyl-p-tolyliodonium bromide and phenyl-p-anisylidonium bromide with lithium 2-nitropropan-2-ide. Simultaneous occurrence of electron transfer initiated radical cage collapse and chain mechanisms have been proposed for the formation of arylated nitroparaffins on one hand and aromatic hydrocarbons, biaryls and formaldehyde on the other.

The reactions of arenediazonium fluoroborates, viz. benzene-diazonium fluoroborate, p-nitrobenzenediazonium fluoroborate and p-methoxybenzenediazonium fluoroborate with sodium nitrite as well as lithium 2-nitropropan-2-ide form the subject matter of Chapter III. The reactions of arenediazonium cations with ambident nitrite ions have been shown to occur via a radical nucleophilic substitution mechanism initiated by a single

electron transfer from the nitrite ion to the π^* MO of the arene-diazonium cation. A similar autoinitiated electron transfer mechanism in which free radicals intervene has been proposed for the reaction of highly oxidizing p-nitrobenzenediazonium fluoroborate with ambident 2-nitropropanate anion. A new example of an entrainment process in the Cu(I) induced electron transfer free radical reactions of benzenediazonium cation and p-methoxybenzenediazonium cation with 2-nitropropanate anion has been identified.

In Chapter IV, the reactions of five arenediazonium fluoroborates $p\text{-R-C}_6\text{H}_4\text{-N}^+\text{NBF}_4^-$ (R = H, NO_2 , CH_3O , CH_3CO and CH_3) with benzylmagnesium chloride as well as tert.butylmagnesium chloride have been examined in detail. The major mechanistic pathway in these reactions has been found by chemical and ESR studies to involve an electron transfer from the Grignard reagent to the π -system of the arenediazonium cation. Radicals have been found to serve as the immediate precursors of the final products.

Studies on the reductive demercuration and symmetrization of a few organomercuric halides, viz. benzylmercuric chloride, phenylmercuric chloride, p-tolylmercuric chloride and p-nitrophenylmercuric chloride with sodium naphthalene as well as lithium aluminium hydride, constitute the subject matter of Chapter V. Novel electron transfer free radical mechanisms have been elucidated for these reactions.

A summary of the main results and conclusions constitutes the subject matter of Chapter VI. Most of the work described in this thesis has been summarized in the undermentioned papers,

some of which have also been discussed at National and International conferences.

- (1) P.R. Singh, Ramesh Kumar and R.K. Khanna, "Radical nucleophilic substitution mechanism in the reactions of arene-diazonium cations with nitrite ions," *Tetrahedron Letters*, 23 (49), 5191 (1982).
- (2) P.R. Singh and R.K. Khanna, "Simultaneous occurrence of electron transfer initiated radical cage collapse and chain mechanisms in the reactions of diaryliodonium cations with 2-nitropropanate anion," *Tetrahedron Letters*, 23 (50), 5355 (1982).
- (3) P.R. Singh, R.K. Khanna and B. Jayaraman, "Electron transfer free radical mechanisms in the reactions of arenediazonium cations with Grignard reagents," *Tetrahedron Letters*, 23(51), 5475 (1982).
- (4) P.R. Singh and R.K. Khanna, "Simultaneous occurrence of electron transfer initiated radical cage collapse and chain mechanisms," *Handbook, 3rd International Symposium on Free Radicals, Freiburg, West Germany, August 1981*, pp. 234.
- (5) R.K. Khanna and P.R. Singh, "Sodium naphthalene induced symmetrization of arylmercuric halides," *Handbook, Sixth National Symposium on Organic Chemistry, Calcutta, India, March 1982*, paper No. CP.15, p. 20.
- (6) P.R. Singh, R.K. Khanna and B. Jayaraman, "Electron transfer free radical mechanisms in the reactions of arenediazonium salts with Grignard reagents," *Bull. Soc. Chim. Belg.*, 91, 458 (1982); *Proceedings, Sixth IUPAC Conference on Physical Organic Chemistry, Louvain-LA-Neuve, Belgium, July 1982*.
- (7) P.R. Singh and R.K. Khanna, "Sodium naphthalene induced reductive demercuration and symmetrization of organomercuric halides," *Tetrahedron Letters*, 24, 000 (1983); Accepted.

- (8) P.R. Singh and R.K. Khanna, "Electron transfer mechanism in lithium aluminium hydride reduction of organomercuric halides," Tetrahedron Letters, Communicated (December 1982).

It is suggested that the importance as well as occurrence of electron transfer reactions involving radical anion intermediates in organic chemistry and also in biochemistry may be much more than previously ever thought.

Particular care has been taken to give due credit to the work reported by other authors in the literature. The author is fully responsible for purely unintentional oversights and errors which could be traced herein.

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CHAPTER I

ELECTRON TRANSFER PROCESSES AND RADICAL-ANION INTERMEDIATES

I.1 Introduction

Electron transfer processes and radical-anion intermediates in organic reactions have been known for well over a century. The first report on radical-anions by Berthelot¹ and the subsequent observation made by Bechman and Paul² on their existence, went unacclaimed for over fifty years. The statement made by Kenner^{3a} that "radicals rather than ions are produced more frequently than is usually realized" and his suggestion^{3b} in 1945 that organic reactivity should be recognized in terms of oxidation and reduction processes, was not given due attention until about fifteen years back when Professors G.A. Russell, N. Kornblum and J.F. Bunnett provided experimental evidence in

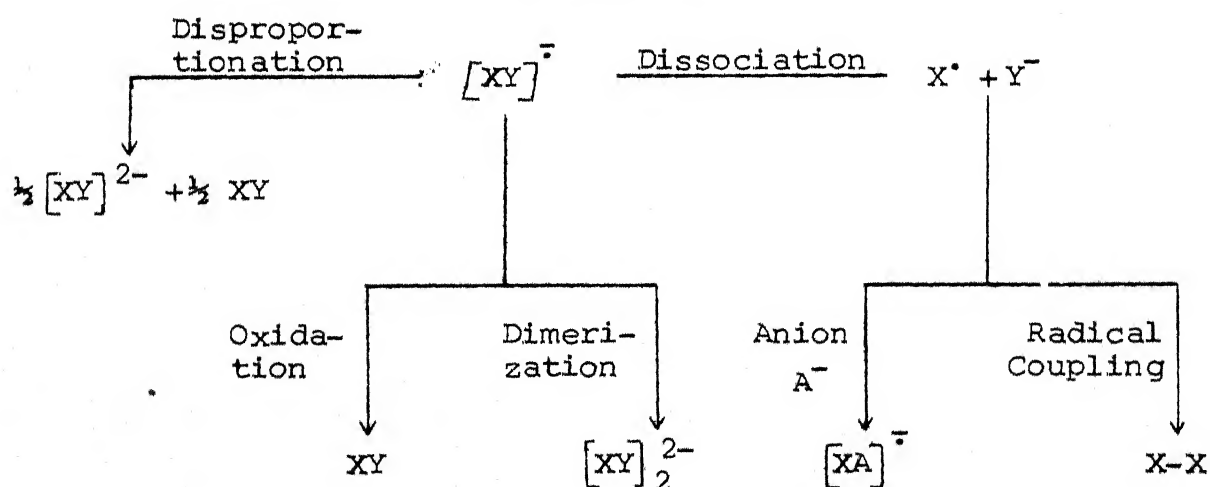
favour of electron transfer processes involving radical-anion intermediates in several reactions formally classified under nucleophilic displacements. Since then, pioneering researches of Professors M. Szwarc, G.D. Sargent, J.K. Kochi, W.A. Pryor, S. Bank, J.F. Garst, R.O.C. Norman, E.C. Ashby, A.J. Birch, H.O. House, J.A. Wolfe, J.A. Marshall, R.A. Rossi and several other eminent scientists have significantly contributed to this fast developing area of immense chemical and biochemical interest.

A chemical, photolytic or electrolytic single electron reduction of an appropriate molecule may lead to the formation of a radical-anion (Eq. 1):



The new odd electron species with an overall negative charge, may undergo various types of reactions outlined in Scheme I.1:

SCHEME I.1



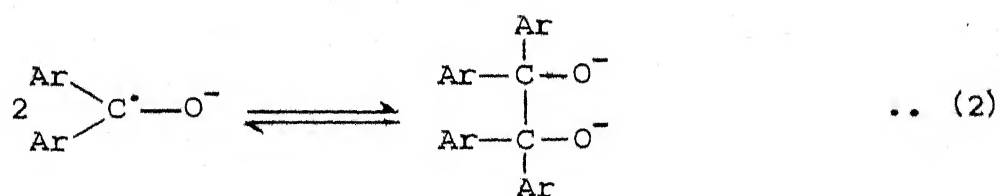
A wide variety of chemical species are known to act as donors in electron transfer reactions. For example, metals,⁴⁻¹³

organometallic reagents and carbanions,¹⁴⁻²⁵ anions,²⁶⁻³² metals in their lower oxidation states,³²⁻⁴⁰ Lewis bases,⁴¹⁻⁴⁷ and alkyl radicals,^{40,48-51} are known to transfer electrons to appropriate substrates. Carbonium ions,⁵²⁻⁵⁴ metal ions in their higher oxidation states,^{35,55-57} aromatic hydrocarbons,^{5b,58-64} molecules with electronegative substituents,⁶⁵⁻⁶⁷ and radicals^{7,68,69} accept electrons to produce corresponding radicals, metal ions in lower oxidation states, radical-anions or anions, when energy requirements are satisfactorily met.

Production of radical-anions and their reactions have been extensively reviewed.⁷⁰⁻⁸² Recently ESR,⁸³⁻⁸⁶ UV,^{87,88} and CIDNP⁸⁹ studies have gained popularity as important tools for the investigation of radical-anions.

I.2 Reductions via Single Electron Transfer From Metals

The observation of an intense blue coloration in the reaction of sodium metal with benzophenone under nitrogen atmosphere first by Bechman and Paul² formed the basis of extensive studies on metal ketyls. The free radical nature of metal ketyls was established by subsequent investigations.⁹⁰⁻⁹⁷ Magnetic susceptibility measurements^{94,95,97} led to the conclusion that ketyl radicals are in equilibrium with diamagnetic pinacolate species (Eq. 2):



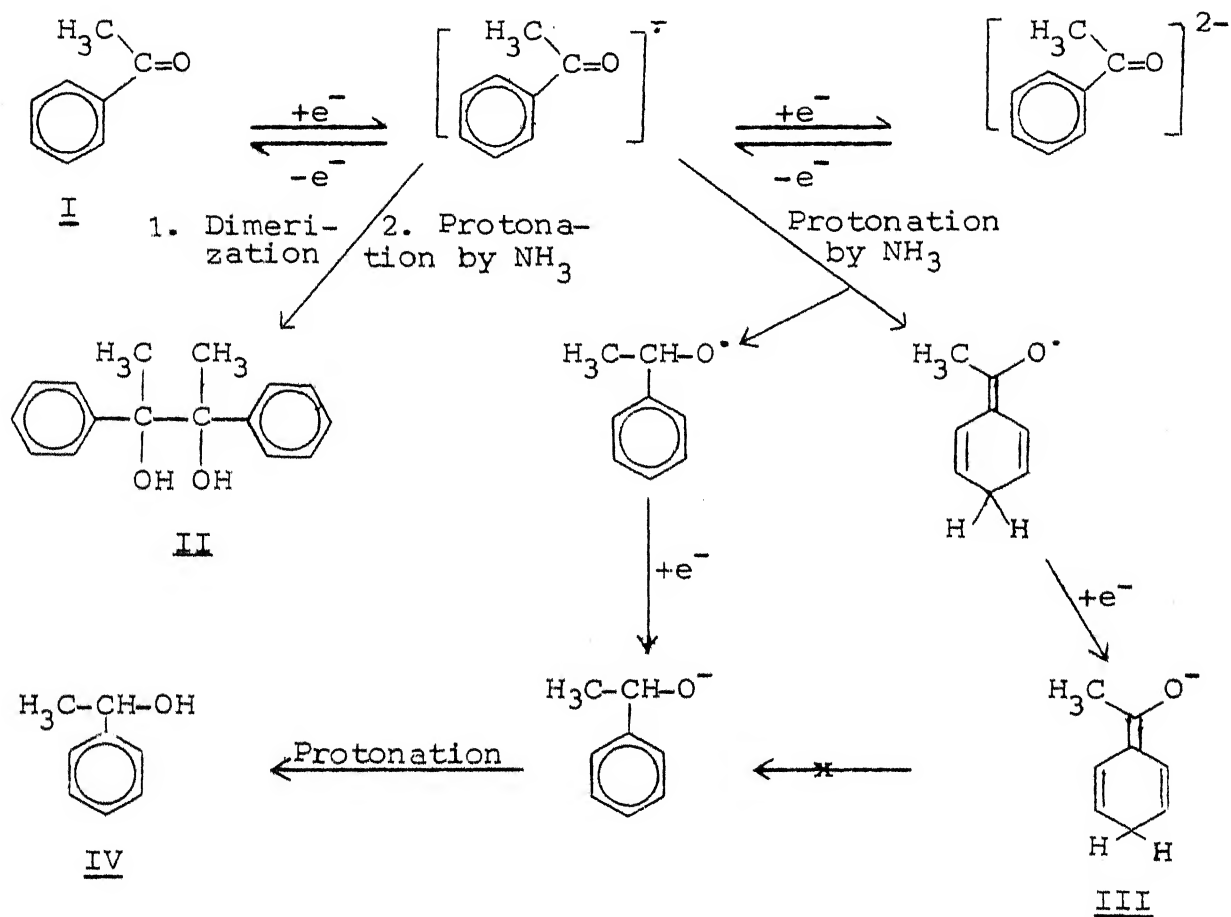
Now a wide variety of organic substrates⁹⁸⁻¹⁰⁴ are known to be reduced by solutions of alkali metals, as well as calcium, magnesium, zinc and iron in liquid ammonia,^{105,106} low molecular weight amines¹⁰⁷⁻¹⁰⁹ or ethers like DME and THF.¹¹⁰ Such reactions are now understood as internal electrolytic reductions¹¹¹ in which an electron is transferred from the metal surface or the metal in solution to the organic molecule under consideration.

Reduction of several organic compounds of the type >C=X , where X can be N-, O, C \searrow and S, has been accomplished by the use of alkali metal/solvent reagents. Radical-anions and monomeric and dimeric dianions are formed in these reductions, which undergo further transformations to yield the products. For example, the reduction of acetophenone I¹¹² with lithium in liquid ammonia gives 2,3-diphenylbutane-2,3-diol II, 1-(cyclohexa-2,5-dienylidene)enolate III and 1-phenylethanol IV as shown in Scheme I.2.

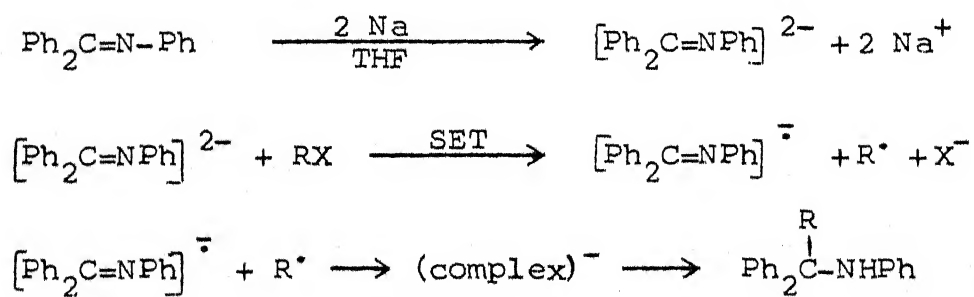
The monomeric dianions formed in the reduction of a -C=N- bond¹¹³⁻¹¹⁵ by alkali metals in protic solvents, not only act as nucleophilic reagents,^{113a} but also participate in electron transfer processes.^{113b} This is illustrated by the reaction of benzophenone anil and alkyl halides in the presence of Na/THF which is believed to proceed as outlined in Scheme I.3.

Similar reactions with dianions of thiocarbonyl compounds¹¹⁶ and olefins^{117,118} are also known to occur.

SCHEME I.2

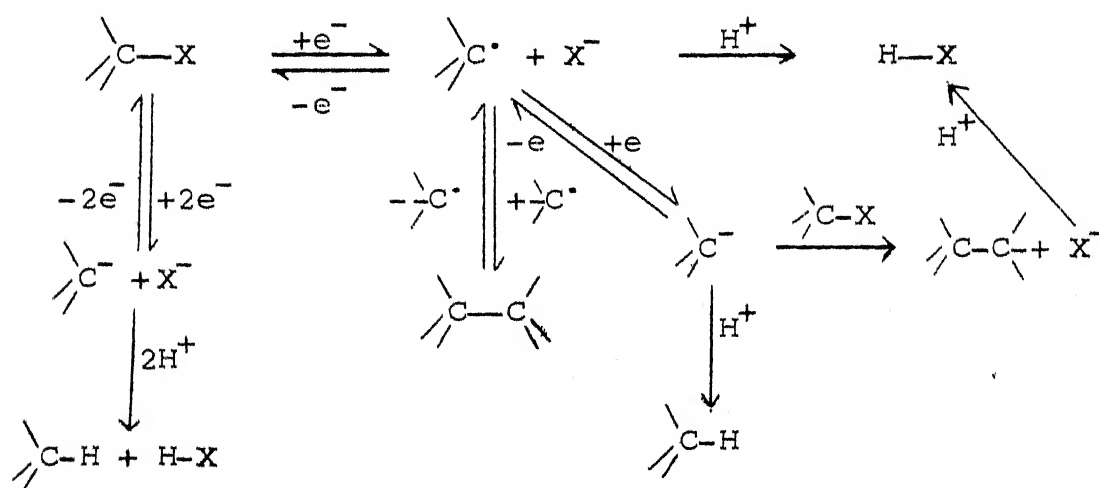


SCHEME I.3

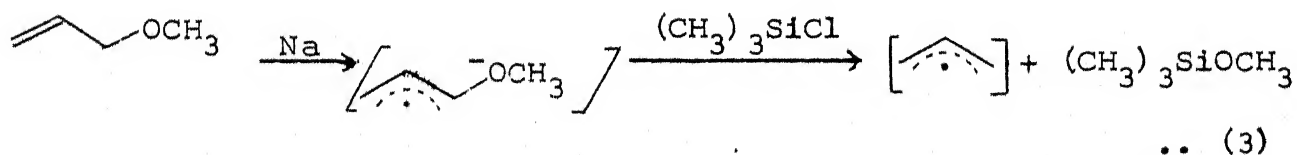


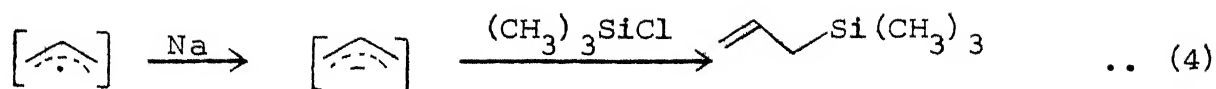
One of the most important reactions of alkali metal/solvent reductions is the reductive cleavage of compounds of the type >C-X , where X may be OH, OR, ONO_2 , CR_3 , SR or a halogen. A possible mechanistic sequence for such reductions is outlined in Scheme I.4:

SCHEME I.4

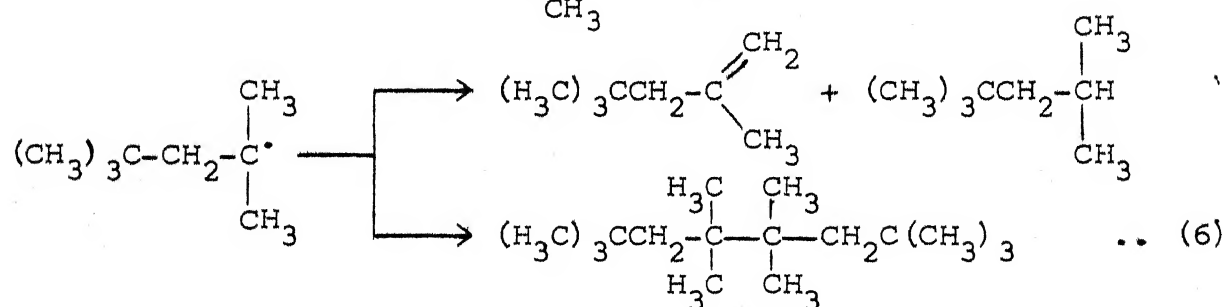
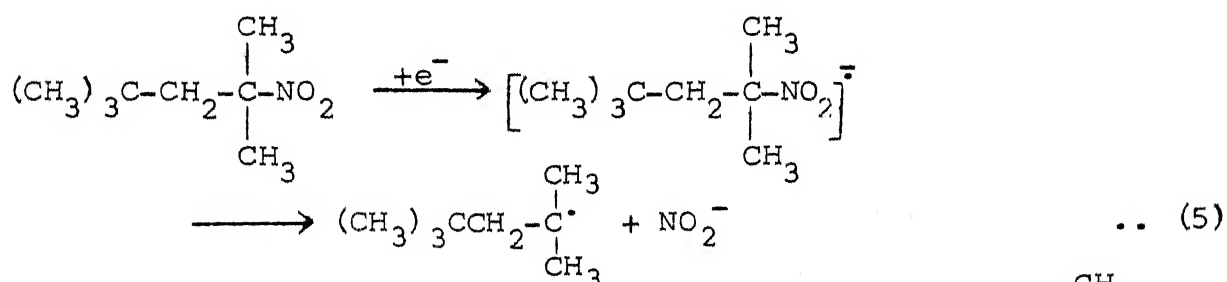


Recent reports on the reductive cleavage of C-O,¹¹⁹ C-C,¹¹⁹⁻¹²¹ C-Cl,¹²² and C-S¹²³ bonds are in conformity with the above mechanism. Tzeng and Weber¹²⁴ have recently reported the cleavage of allylic and benzylic methyl ethers by sodium metal. The pathway, for the reaction of allylmethyl ether in the presence of trimethylchlorosilane is illustrated by Eqs. 3 and 4:





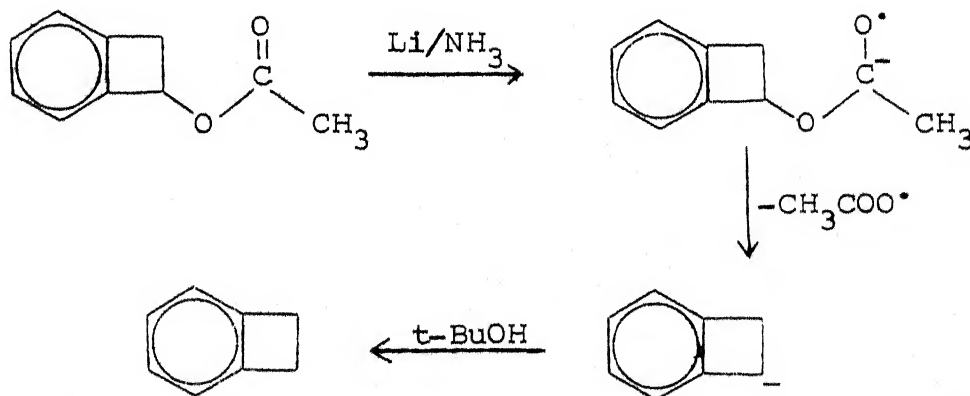
On treatment with sodium,^{101a} 2,4,4-trimethyl-2-nitropentane gives a mixture of hydrocarbons as shown in Eqs. 5 and 6:



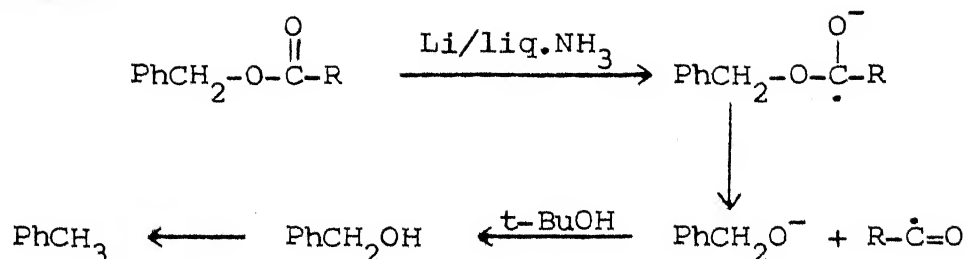
Esters also undergo cleavage via electron transfer. Thus, Li/liq. NH_3 affects the cleavage of esters,^{120a,125} by one of the two pathways exemplified in Scheme I.5:

SCHEME I.5

1st pathway:



2nd pathway:



I.3 Reactions of Radical-Anions of Aromatic Hydrocarbons

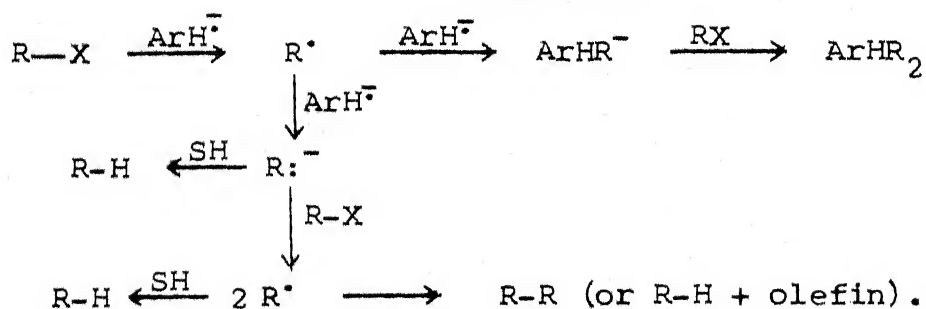
Alkali metals reduce aromatic hydrocarbons¹²⁶⁻¹²⁸ producing radical-anions. Thus, reduction of naphthalene¹²⁹ by sodium yields sodium naphthalene (Eq. 7):



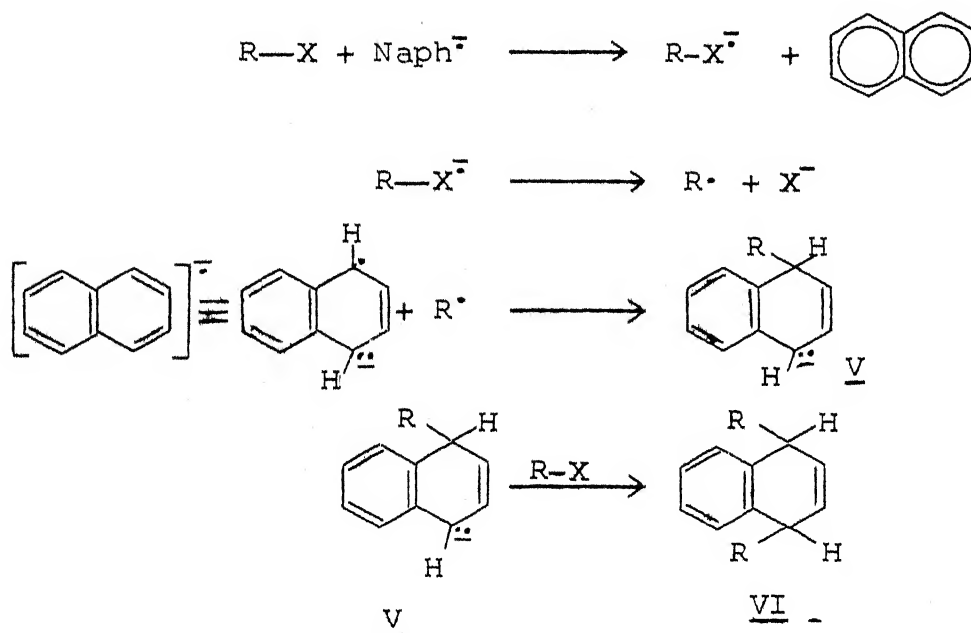
These radical-anions can either act as strong bases and abstract protons from weakly acidic substrates or transfer a single electron to appropriate substrates.

Reactions of alkyl halides with aromatic radical-anions have been thoroughly investigated and reviewed.¹³⁰⁻¹³² The general mechanism of these reactions is outlined in Scheme I.6:

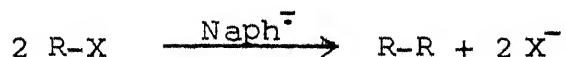
SCHEME I.6



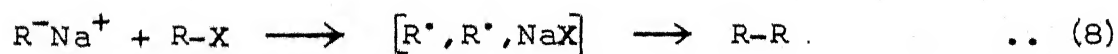
Alkylation of aromatic nucleus proceeds by coupling of alkyl radicals with aromatic radical-anions. For example, reaction of sodium naphthalene with R-X first produces anion V which, by subsequent S_N2 displacement on the alkyl halide gives dialkylate^{133,134} VI :



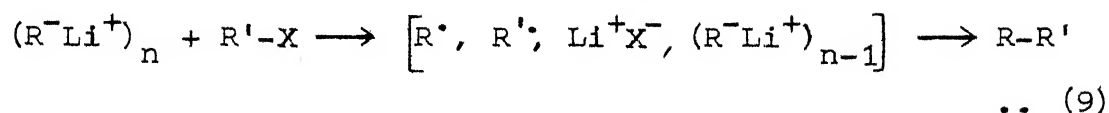
Of various reactions of alkyl halides, reductive dimerization is the least understood:



Both radicals¹³⁵ and anions¹³⁴ are proposed as intermediates in the formation of dimers. The most acceptable explanation for the rapid rate of alkyl dimer formation is the coupling of geminate radical pairs¹³⁴ as shown in Eq. 8:

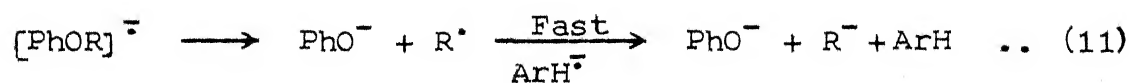


In this respect, the above reaction is parallel to that of alkyl lithiums with alkyl halides (Eq. 9):



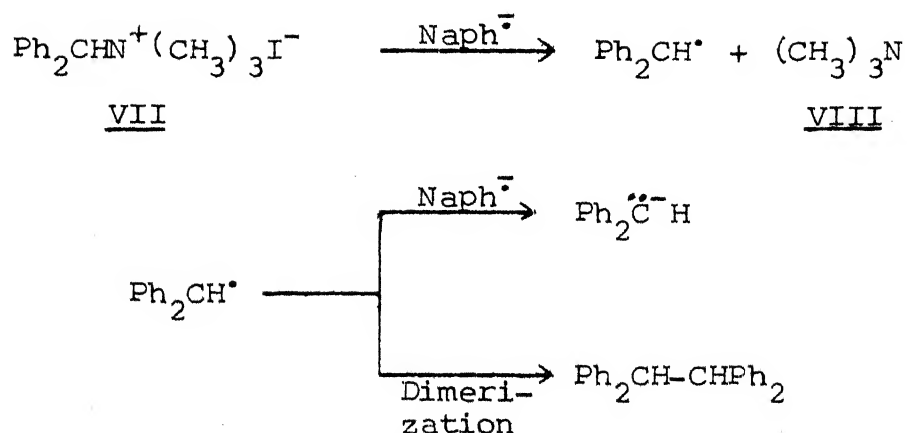
The radical pairs generated by electron transfer from alkyl-lithium in solvent cage, may couple, disproportionate or diffuse apart. The intermediate radicals formed in this reaction have been trapped¹³⁶ and detected by ESR spectroscopy.^{137,138} Dimerization has also been observed in the reduction of alkyl halides with metal complexes.¹³⁹ Cyclopropyl halides are also reduced by alkali metal naphthalenes.¹⁴⁰

Ethers have been cleaved with radical-anions of aromatic hydrocarbons.¹⁴¹⁻¹⁴⁴ The general sequence of steps are shown in Eqs. 10 and 11:

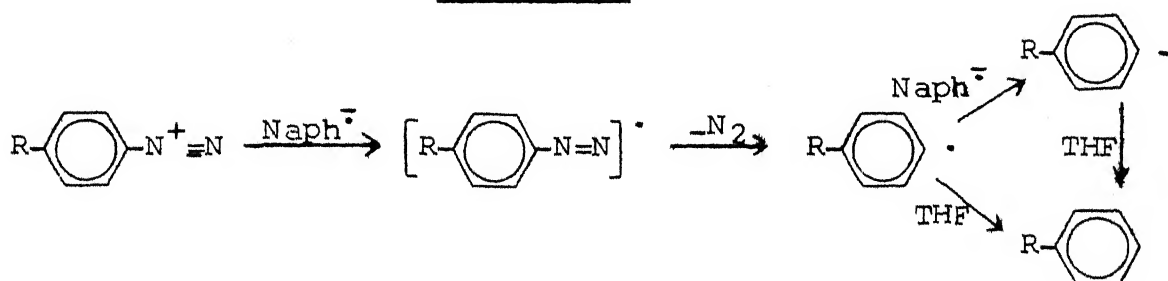


The O-S bond in toluene sulfonates^{145,146} and N-S bond in N-substituted sulfonamides¹⁴⁷ also cleave by a similar pathway.

Scission of C-N bond in quaternary ammonium salts VII¹⁴⁸ to give tertiary amines VIII and benzylic dimers has been affected by sodium naphthalene radical-anion as shown in Scheme I.7:

SCHEME I.7

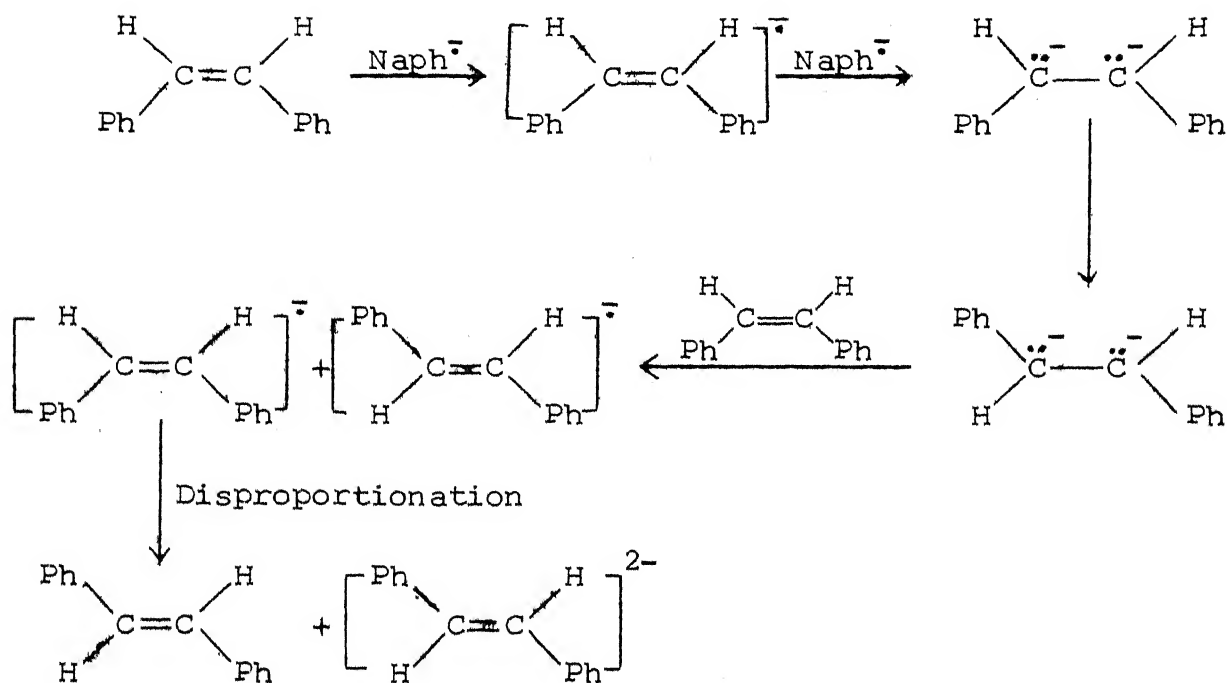
Singh and coworkers¹⁴⁹ have proposed a $\pi^*-\pi^*$ electron transfer mechanism involving the intervention of aryl radicals in the dediazonium of arenediazonium salts with sodium naphthalene (Scheme I.8):

SCHEME I.8

Sodium naphthalene also reacts with phenylacetonitrile^{150,151} to give a mixture of products.

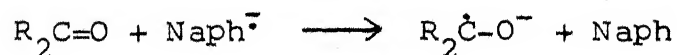
Sodium naphthalene induces isomerization of Z stilbene to E stilbene,¹⁵² via the dianion shown in Scheme I.9. Sodium naphthalene induced reductive cleavage of esters has also been reported recently.^{122,153}

SCHEME I.9

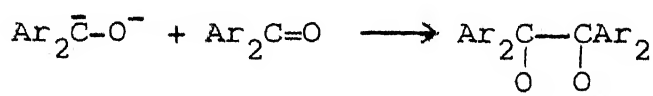
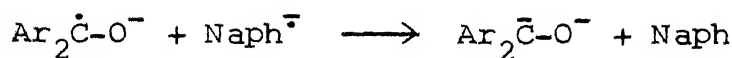
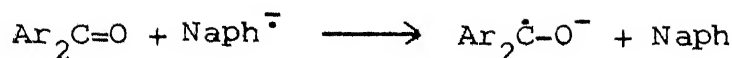
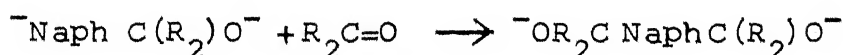
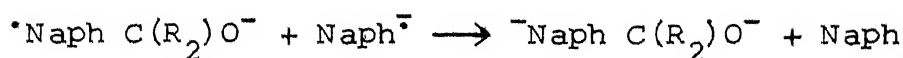
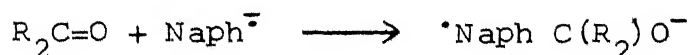
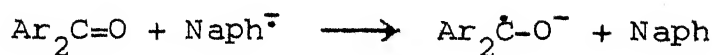


Holy and coworkers¹⁵⁴ have proposed two alternative mechanisms, one involving dianion intermediates and the other free radicals, in the reaction of aliphatic and aromatic ketones with sodium naphthalene (Scheme I.10):

SCHEME I.10

(A) Dianion Mechanism(1) Aliphatic carbonyl compounds:

...contd.

(ii) Aromatic carbonyl compounds(B) Radical Mechanism(i) Aliphatic carbonyl compounds(ii) Aromatic carbonyl compounds

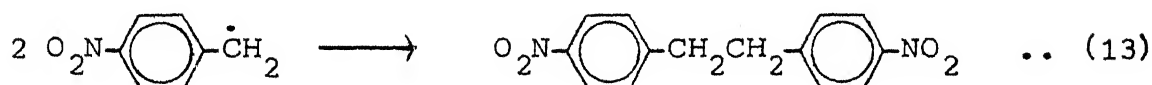
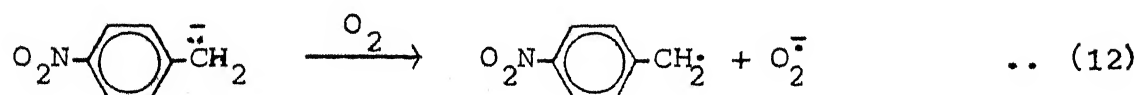
Sodium naphthalene also reacts with molecular hydrogen,¹⁵⁵ sulfur dioxide,¹⁵⁶ carbon dioxide,¹⁵⁷ arylhalosilanes¹⁵⁸ and arylphosphates.¹⁵⁹ Naphthalene radical-anions have been effectively used to initiate polymerization reactions^{160,161} and in the fixation of molecular nitrogen.¹⁶²

I.4 Organic and Inorganic Anions as Donors in Non-Chain Electron Transfer Processes

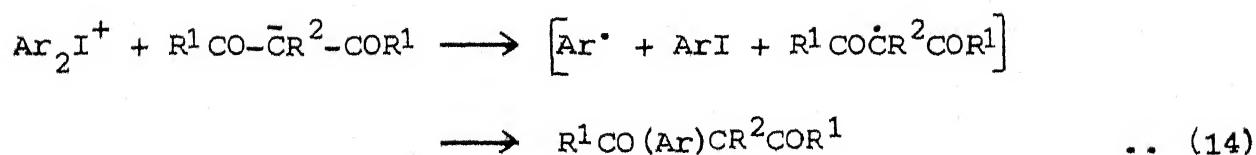
Several organometallic reagents and anions including carbanions, react with suitable electron acceptors by single

electron transfer mechanisms. In 1916 Schlenk¹⁶³ reported the formation of benzophenone ketyl by the reduction of benzophenone with triphenylmethyl carbanion. Later, various other anions, like tert.butoxide anion and 2,4,6-tri-tert-butylphenoxide anion, were demonstrated to transfer electrons to several other substrates.^{54,72,164} Aromatic nitro compounds, when treated with anions,¹⁶⁵⁻¹⁶⁸ are known to form radical-anions.

Oxidative dimerization of carbanions has been affected with various oxidizing agents.^{165,168} Thus, p-nitrobenzyl carbanion transfers an electron to molecular oxygen resulting in the formation of a dimeric product (Eqs. 12 and 13):



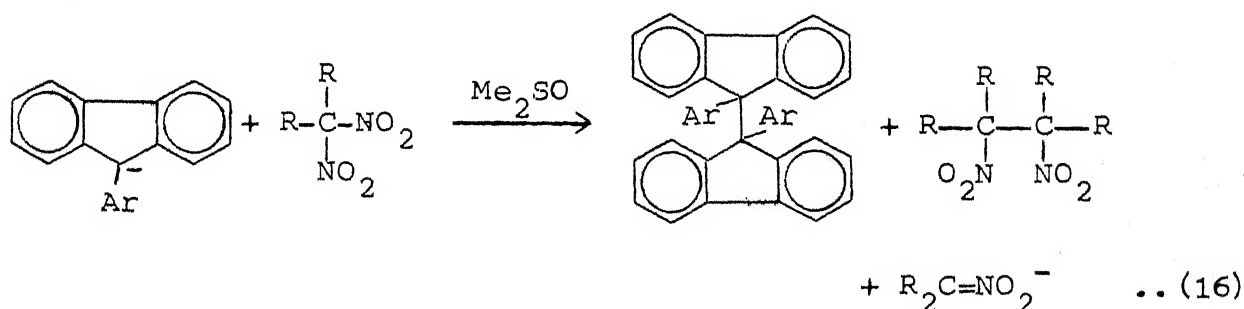
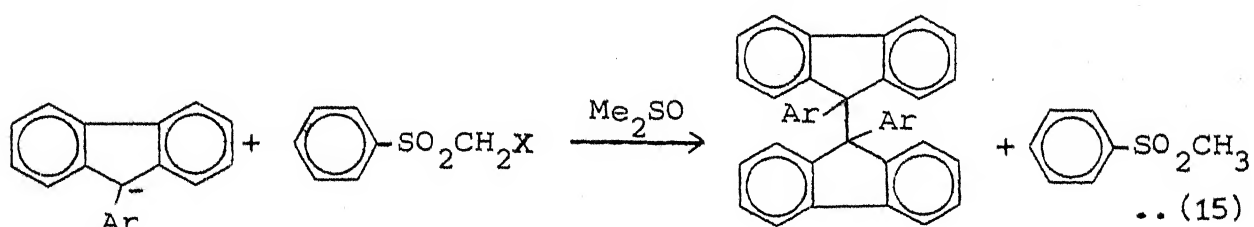
An electron transfer cage collapse process has been proposed in the phenylation of carbanions by iodonium salts.¹⁶⁹ Thus, enolate anions are phenylated by iodonium salts, as shown in Eq. 14:



Reactions involving electron transfer from thiophenoxide^{31a,170-172} and alkoxide¹⁷³ anions have also been reported. An electron

transfer from a donor reagent is feasible only when the substrate has sufficiently high electron affinity. This explains the inability of butyl lithium¹⁷⁴ to add to tetraphenyl ethylene or 1,1,3,3-tetraphenyl but-1-ene as also the successful oxidation of even poor donors like alkoxides¹⁷⁵ by aromatic nitro compounds.

Recently, single electron transfer has been proposed in the reactions of 9-arylfluorenyl anions with phenyl halomethyl sulfones and dinitro compounds¹⁷⁶ (Eqs. 15 and 16):

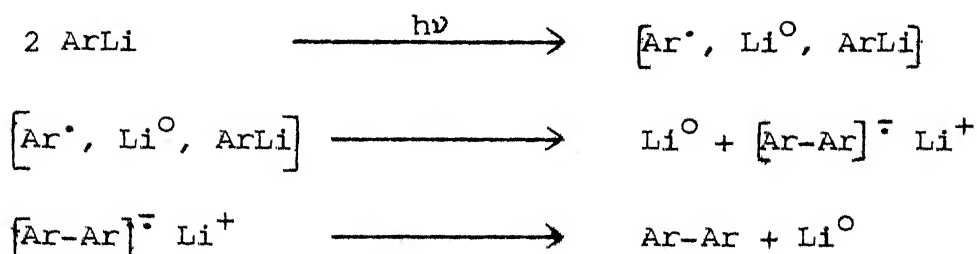


Straight line Bronsted correlations of the pK_a 's of the fluorenyl system vs. the observed rates of these reactions, were interpreted as showing that stronger bases give up electrons more readily.

Organolithium compounds are known to donate electrons to aromatic hydrocarbons,¹⁷⁷ oxygen,⁷⁹ and peroxides.¹⁷⁸ Biphenyl radical-anion has been proposed as an intermediate in the

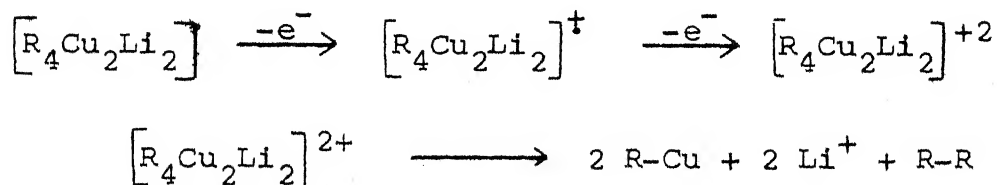
photolysis of phenyllithium by van Tamelen and coworkers¹⁷⁹
(Scheme I.11):

SCHEME I.11



Lithium organocuprates add to unsaturated carbonyl compounds¹⁸⁰ by an electron transfer mechanism. Oxidation of lithium organocuprates by O_2 , PhNO_2 or Cu(II) salts, yielding dimers, proceeds by a two-electron oxidation pathway (Scheme I.12):

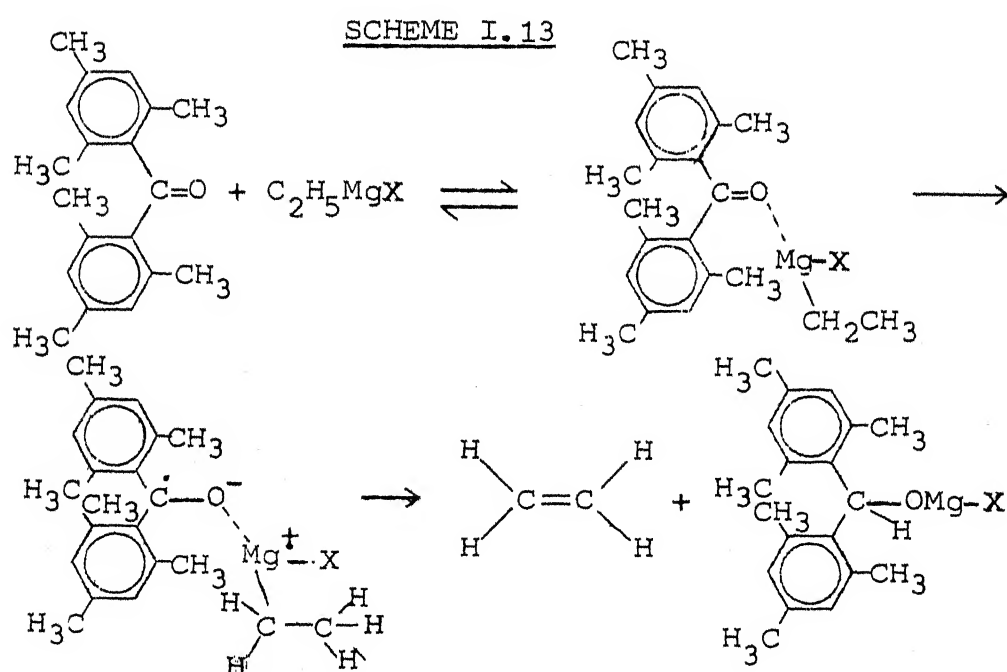
SCHEME I.12



Lithium 1,1-dimethylallene, prepared by the reaction of 1,1-dimethylallene with lithium tetramethylpiperidine, has been shown to react with benzyl chloride¹⁸¹ and ketones¹⁸² by single electron transfer pathways.

Reactions of Grignard reagents with various substrates have been found to proceed via SET mechanisms. Electron transfer from Grignard reagents to oxygen,¹⁸³ ketones,^{14-16,19} alkyl halides²² and non-benzenoid aromatic compounds has been

reported. Following earlier leads concerning the behaviour of Grignard reagents and dialkyl magnesium compounds,¹⁸⁴⁻¹⁸⁶ Ashby and coworkers have used radical probes to investigate the role of electron transfer in Grignard reagent addition to ketones.¹⁸⁷⁻¹⁸⁹ Thus, sterically hindered ketones are reduced to alcohols via a SET process¹⁹⁰ as shown in Scheme I.13:

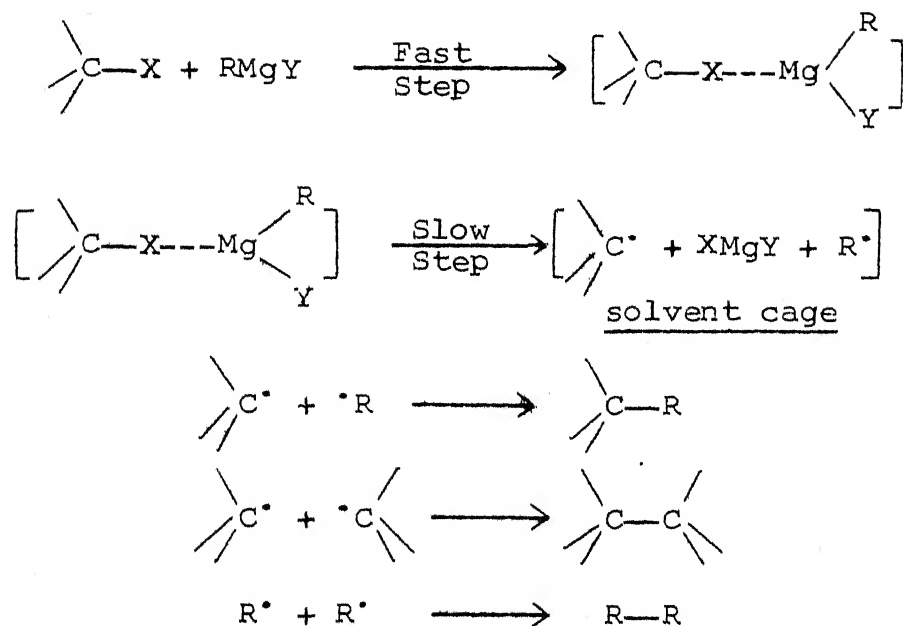


The spectroscopic evidence obtained suggests that the rate of electron transfer from the Grignard reagent, to the ketone is a function of the number of β -hydrogen atoms present in the alkyl group of the Grignard reagent, rather than the previously suggested stability of the intermediate alkyl radical.

Singh and coworkers²² have proposed electron transfer as the first step in the reaction of Grignard reagents with benzylic

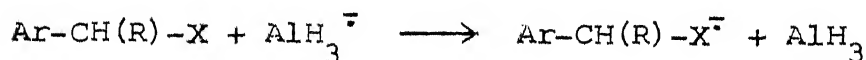
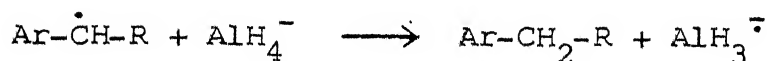
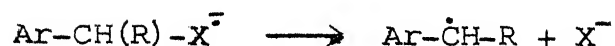
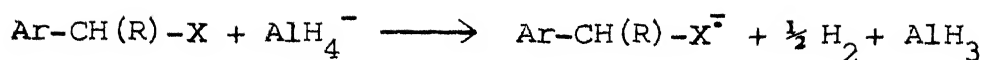
halides as shown in Scheme I.14:

SCHEME I.14



Recently, reactions of (9-anthryl)arylmethyl chlorides with organomagnesium and lithium reagents have been shown to proceed via single electron transfer pathways.¹⁹¹

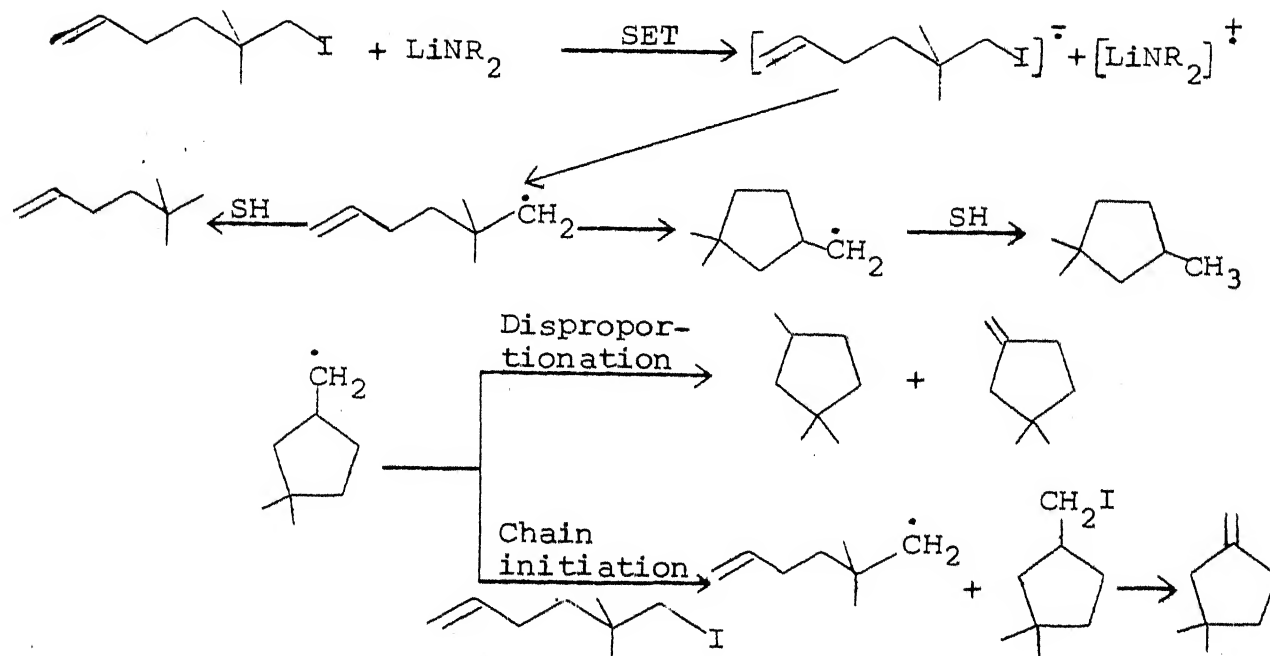
Several metal hydrides (e.g., LiAlH_4 , AlH_3 , MgH_2 etc.) reduce ketones,¹⁹² polynuclear aromatics,¹⁹³ bromophenylallyl ether¹⁹⁴ and alkyl halides¹⁹⁵ by a single electron transfer process. Lithium tetrakis(N-dihydropyridyl)aluminate (LDPA) has also been found to give similar results.¹⁹⁶ Recently, a new electron transfer mechanism has been proposed by Singh et al. in the LiAlH_4 reductions of certain benzylic halides¹⁹⁷ and z 2-chlorostilbene.¹⁹⁸ The steps proposed for the reduction of benzylic halides are shown in Scheme I.15:

SCHEME I.15

The halide ion, X^- , formed in step 2, combines with AlH_3 present in the medium giving AlH_3X^- . The latter anion can then either act as a source of hydrogen atoms or donate an electron as an inferior alternative to AlH_4^- . Similarly, anions AlH_2X_2^- and AlHX_3^- formed during the reaction can donate hydrogen atoms or electrons as inferior alternatives to AlH_4^- anion. Quantitative isomerization of Z stilbene to E stilbene in the presence of LiAlH_4 has also been reported to occur via an electron transfer pathway.¹⁹⁸

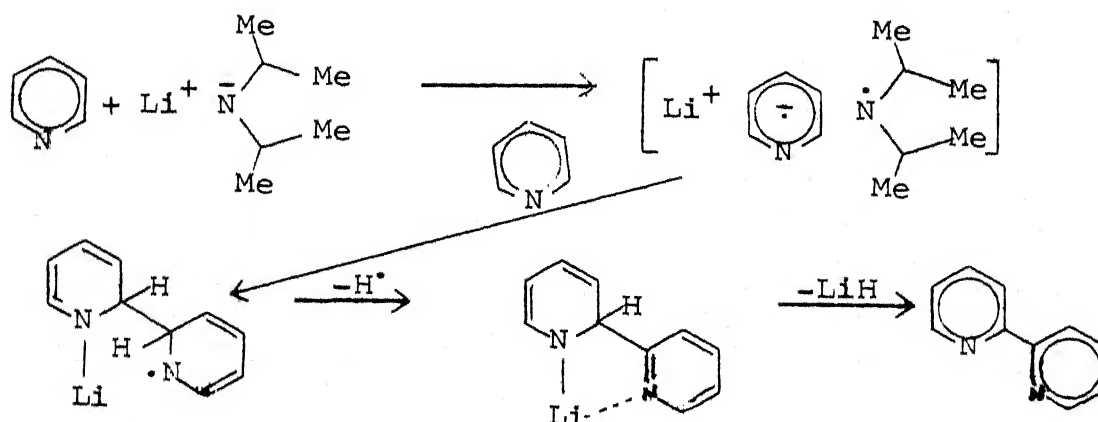
Ashby and coworkers have proposed electron transfer pathways in the reduction of alkyl halides,^{199a} ketones,^{199b} and polynuclear aromatics^{199a} by alkali metal amides and alkoxides.¹⁹⁹ Thus, reduction of alkyl iodides with lithium diisopropylamide proceeds via single electron transfer process outlined in Scheme I.16:

SCHEME I.16



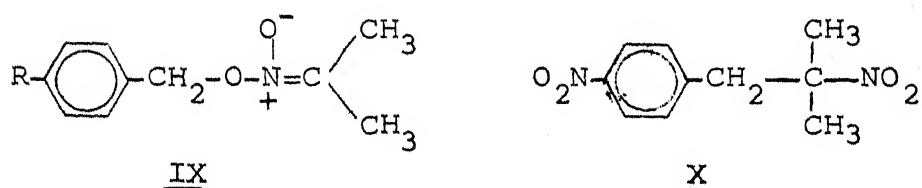
Recently, lithium diisopropylamide has been shown to react also with π -deficient heteroaromatics²⁰⁰ by a single electron transfer mechanism (Scheme I.17):

SCHEME I.17



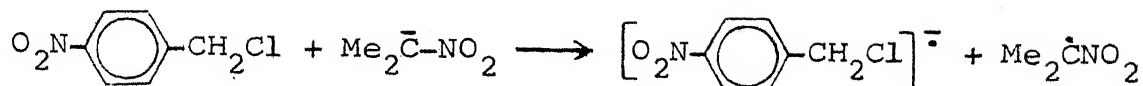
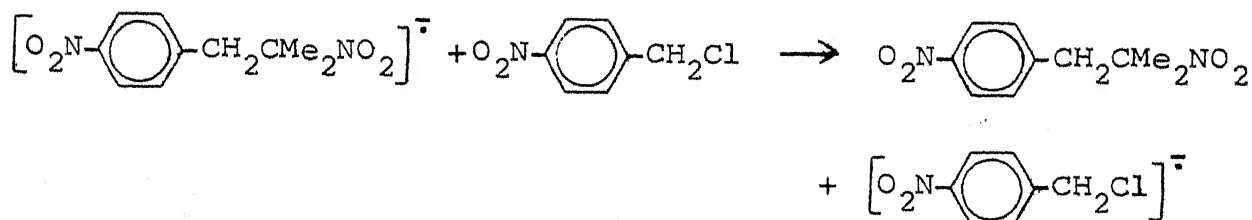
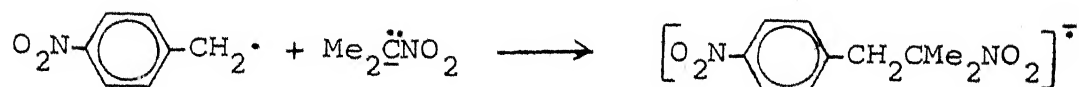
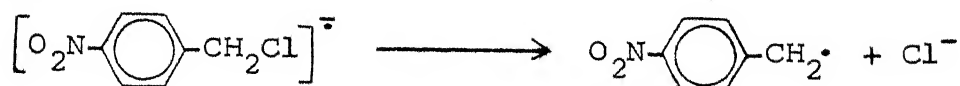
I.5 Electron Transfer Chain Substitution in Aliphatic Compounds: Aliphatic S_{RN}1 Mechanism

Bender and Hass²⁰¹ observed in 1949 that while p-substituted benzyl chlorides, p-R-C₆H₄CH₂Cl (where R = CN, CF₃, ⁺N(CH₃)₃, COCH₃, COOCH₃, CH₃ or Br) on treatment with 2-nitropropanate anion yield O-alkylated products IX, p-nitrobenzyl chloride yields the C-alkylated product X predominantly.



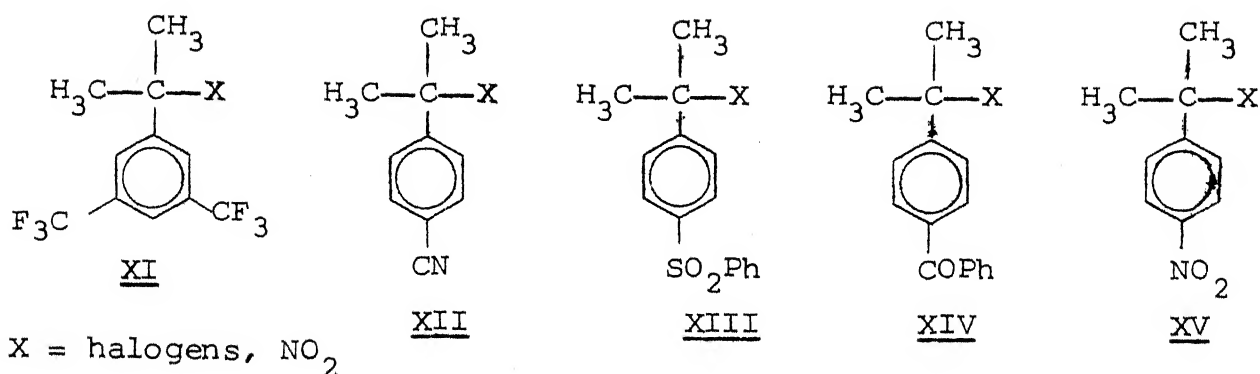
Later, it was found that the ratio of the C- and O-alkylated products depends also on the nature of the leaving group X in the p-nitrobenzyl system p-O₂NC₆H₄CH₂X.²⁰² While the iodide and bromide predominantly give O-alkylated products, the chloride yields C-alkylated product. On the basis of these observations and other detailed studies, it was proposed that O-alkylation proceeds by the usual S_N2 substitution, while C-alkylation is derived from an electron transfer process, in which radical-anions and free radicals are intermediates.^{203,204}

The mechanism for the C-alkylation reaction proposed independently in 1966 by Kornblum et al.^{205,206} and Russell et al.,^{207,208} is outlined in Scheme I.18:

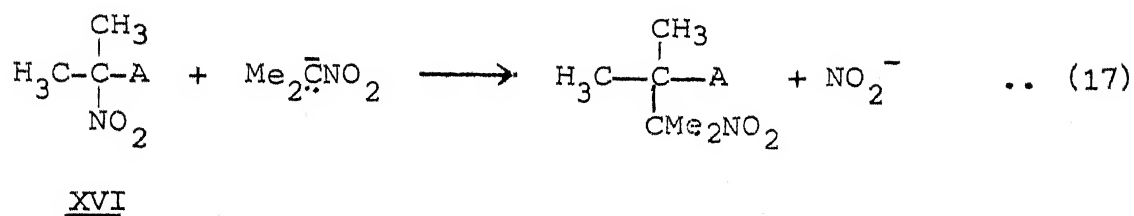
SCHEME I.18Initiation:Propagation:

The radical chain nature of this mechanism was established on the basis of the observations that these reactions are inhibited by oxygen,²⁰⁹ and p-dinitrobenzene²¹⁰ and accelerated by light.^{209,211} A similar mechanism, designated $S_{\text{RN}}1$, was latter proposed by Kim and Bunnett for aromatic systems.²³⁴

The aliphatic $S_{\text{RN}}1$ substitution also takes place at tertiary carbon atoms of p-nitrocumyl chloride,²¹² α -p-dinitrocumene,²¹³⁻²¹⁶ m-nitrocumyl chloride²¹⁷ and α ,m-dinitrocumene²¹⁷ with various nucleophiles. In addition to the p-nitrocumyl system, compounds XI to XV also undergo radical chain substitution reactions with 2-nitropropanate anion.^{80,218}

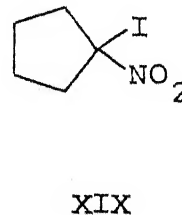
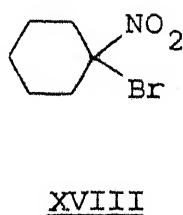
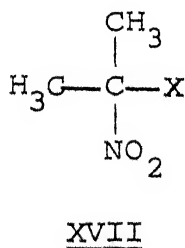


The apparent 'nucleophilic substitution' with 2-nitropropanate anion on purely aliphatic compounds XVI has also been reported to follow a similar S_{RN}1 mechanism^{216, 219, 220} (Eq. 17):



A = COOEt, COPh, CN, NO₂

α-Halonitro compounds XVII — XIX on treatment with nucleophiles undergo substitution in which the halogen rather than the nitro group is displaced.²²¹⁻²²⁵



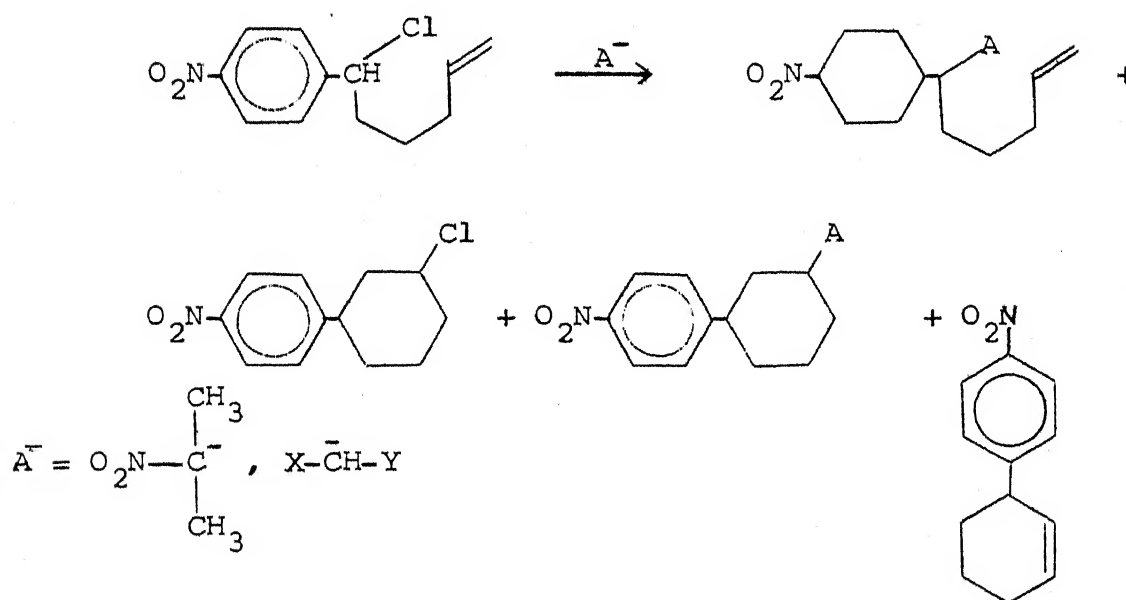
X = Cl, Br, I

Nucleophiles: Me₂C⁻NO₂, EtC⁻(COOEt)₂, Me(CN)C⁻(COOEt)

PhSO₂⁻, , alkyl lithiums.

Displacement of a sulfone group from α -nitrosulfones has been effected by an electron transfer chain mechanism.²²⁶ It has been reported that a cyano group facilitates the electron transfer chain process.²²⁷ α -Nitrosulfides also exhibit $S_{RN}1$ mechanism on reaction with nitronate, malonate and sulfinate anions.^{224a} Intramolecular cyclization using appropriately substituted p-nitrobenzyl chloride²²⁸ has been achieved (Scheme I.19):

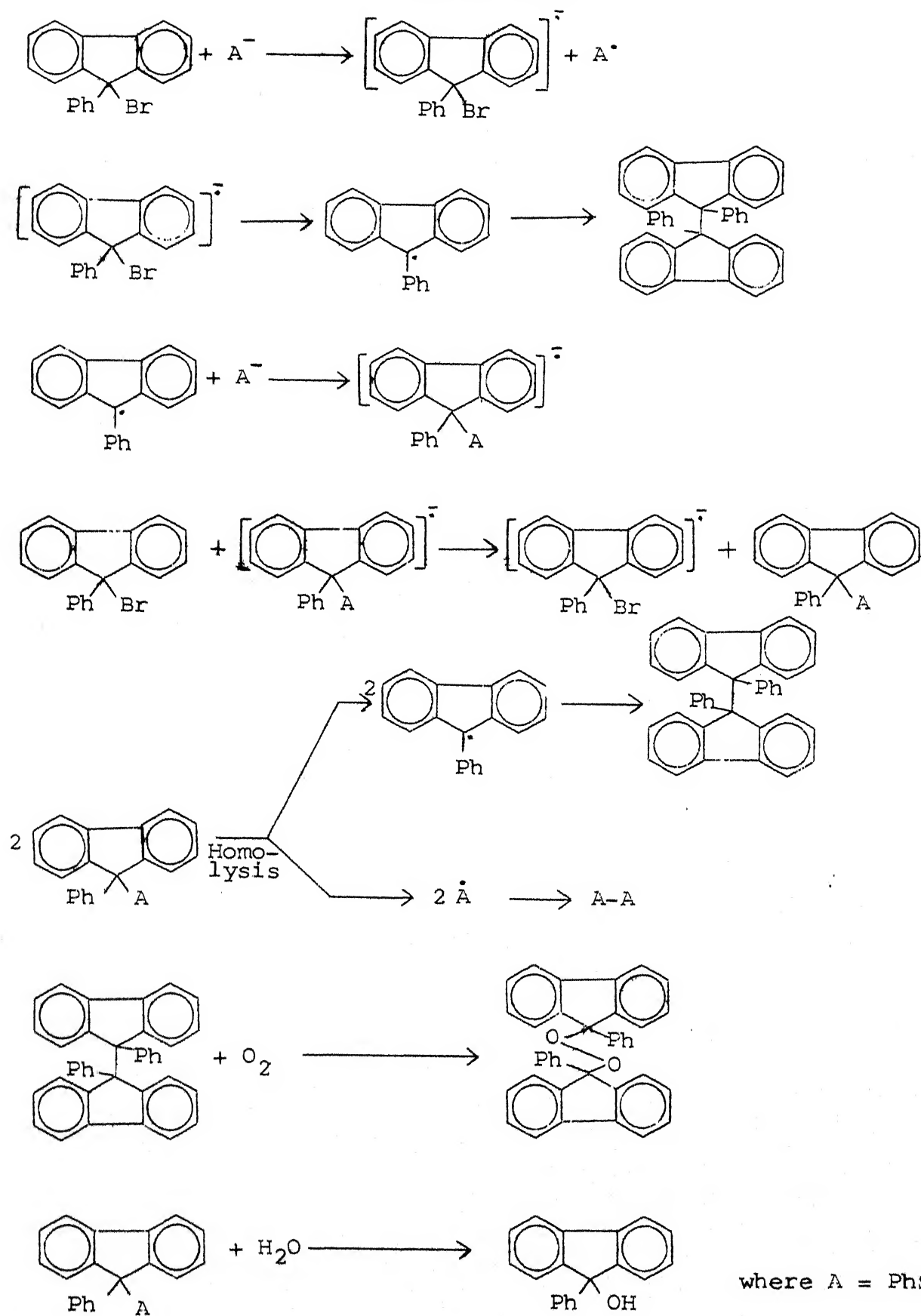
SCHEME I.19



Singh et al.^{31a} have studied the reactions of 9-bromo-9-phenylfluorene with certain nucleophiles and provided evidence in favour of electron transfer radical-anion mechanism outlined in Scheme I.20.

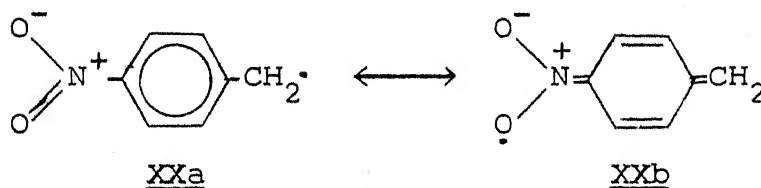
Russell et al. have reported that organomercuric halides react with 2-nitropropanate anion,^{229a} dialkylphosphite anions^{229b} and sulfinate anions²³⁰ by $S_{RN}1$ pathways. Reaction of

SCHEME I.20



N-(p-nitrobenzyl)pyridinium cation with 2-nitropropanate anion²³¹ has also been reported. All these reactions show the characteristics of a chain process involving radical anion intermediates.

Oxyanion nucleophiles do occasionally combine with radicals of the p-nitrobenzyl type in the course of aliphatic $S_{RN}1$ reactions. Kornblum^{218b} has suggested with reference to canonical forms such as XXb, that such steps can be considered as Michael-type attachments of nucleophiles to unsaturated systems. The filled outer shell orbital of the nucleophile interacts with σ^* -orbital at the benzylic radical site.



For tertiary and secondary benzylic systems, Kornblum^{218b} has proposed that the initially formed nitronic esters rearrange to yield more stable C-alkylated products. Norris et al.²³² have recently demonstrated that the regiochemistry of the coupling between p-nitrobenzylic radicals and aci-nitronate ions in the association step is dependent on steric factors. Branching at the carbon which is placed α - to the reaction site causes a shift in product distribution towards O-alkylation and away from C-alkylation. The association step has been proposed to be a kinetically controlled irreversible process.

Recently, a theoretical ab initio study of aliphatic $S_{RN}1$ mechanism has been reported.²³³ This study reveals that the

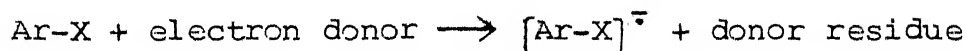
driving force for electron transfer in the initiation step is the spontaneous dissociation of the radical-anion formed and that the propagation rate of the chain mechanism may be determined better by diffusion phenomena rather than by energetic considerations.

I.6 Aromatic Substitution by S_{RN}1 Mechanism

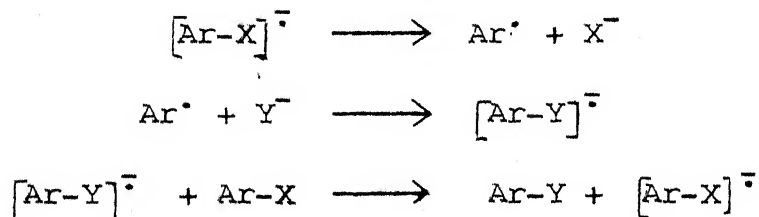
An elegant electron transfer chain mechanism, designated S_{RN}1, in "Aromatic Nucleophilic Substitution Reactions," has been demonstrated by Kim and Bunnett.²³⁴ The generalized version of the mechanism is outlined in Scheme I.21:

SCHEME I.21

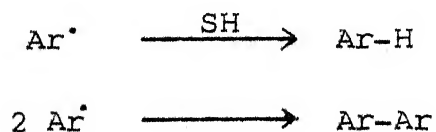
Initiation:



Propagation:



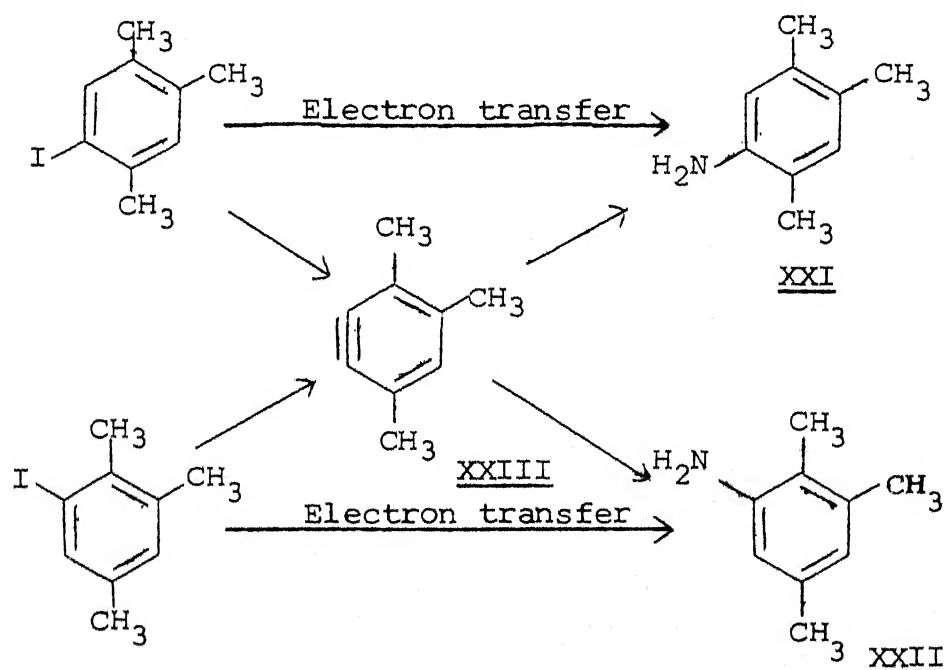
Termination:



The separate components of this radical chain sequence have ample precedents and the overall reaction scheme is analogous

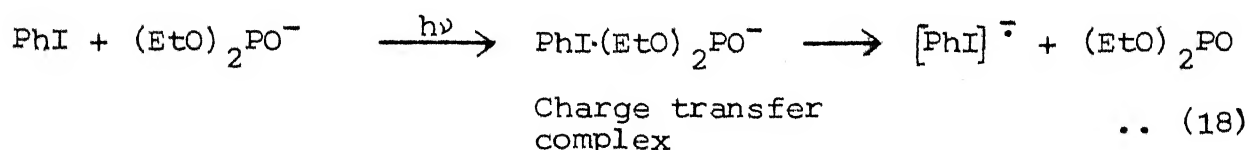
to that proposed earlier by Kornblum²⁰⁵ and Russell²⁰⁷ for substitution in aliphatic systems.

The aromatic $S_{RN}1$ mechanism was postulated for the first time in order to account for the results of the reaction of aryl halides with amide ion in liquid NH_3 .²³⁴ The ratios of the two products XXI : XXII, in the reactions of 5- and 6-iodopseudocumenes with KNH_2 in liquid NH_3 , were found to be dependent on the position of the iodine atom in the starting halide. Aryne intermediate XXIII, if postulated, would yield the two products in the same ratio, in these reactions. This fact coupled with the observed catalysis by light and inhibition of the substitution reaction by tetraphenylhydrazine suggests the occurrence of a radical chain mechanism in these reactions:



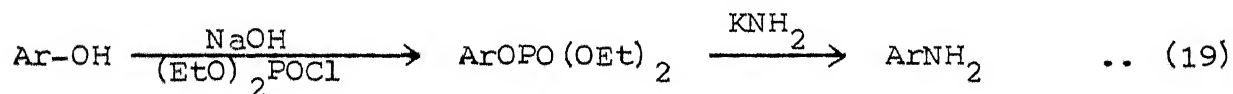
Most aromatic $S_{RN}1$ reactions are initiated either chemically by solvated electrons from alkali metals,²³⁵

electrolytically²³⁶ or photochemically.^{235,237} The exact nature of the photoinitiated process is not known with certainty, but evidence in favour of electron transfer occurring through an intermediate charge transfer complex has been presented (Eq. 18):



The initiation mechanism of the reactions occurring in the dark^{234,238} without addition of electron-donating initiators (the so called autoinitiated reactions) is even more obscure. Here, a reasonable possibility^{205,206} is a thermally activated electron transfer from nucleophile to substrate.

The tendency of the groups SPh ,²³⁹ NMe_3^+ ,²³⁹ and $\text{OPO}(\text{OEt})_2$ ²³⁹⁻²⁴¹ to undergo facile displacement by some other groups via $\text{S}_{\text{RN}}1$ mechanism has great synthetic utility. Thus, Ar-OH can be converted to Ar-NH_2 in good yields²⁴⁰ under mild conditions (Eq. 19):

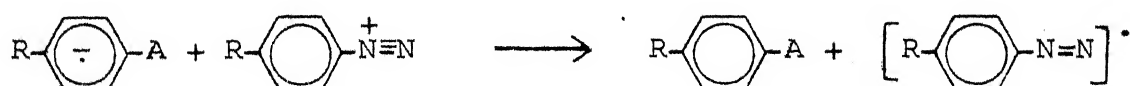
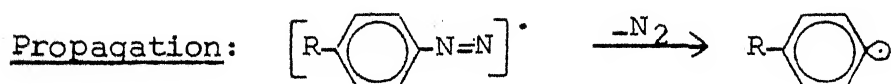
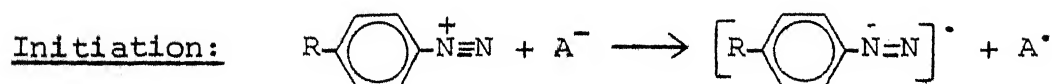


Nucleophiles such as carbanions derived from simple ketones,^{234,239,242-248} nitriles,^{241,246,249} 2- and 4-picoline²⁵⁰ have received much attention with reference to aromatic $\text{S}_{\text{RN}}1$ reactions. Phosphanions, Ph_2P^- ,²⁵¹ $(\text{EtO})_2\text{PO}^-$,²⁵²⁻²⁵⁵ $\text{Ph}(\text{BuO})\text{PO}^-$,²⁵⁶ Ph_2PO^- ,²⁵⁶ $(\text{EtO})_2\text{PS}^-$ ²⁵⁶ and $(\text{Me}_2\text{N})_2\text{PO}^-$ ²⁵⁶

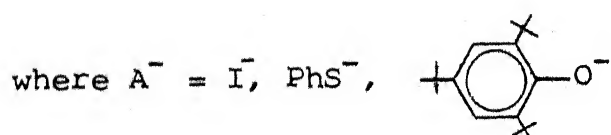
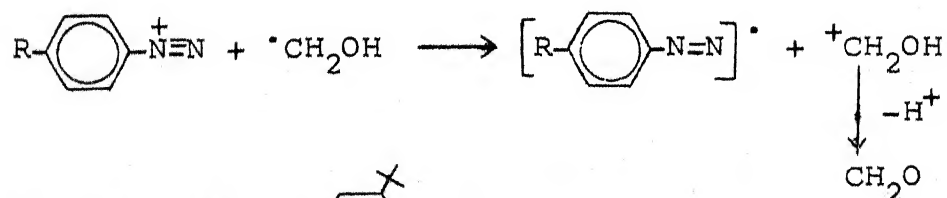
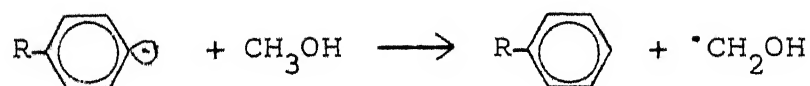
have also been used as electron donors. Among sulfanions arene-thiolates²⁵⁷⁻²⁵⁹ and alkanethiolates^{246,260} have been found to be effective nucleophiles in $S_{RN}1$ reactions. Recently, electron transfer from phenylselenide,²⁶¹ phenyltelluride,²⁶¹ diphenylarsenide,^{262,263} diphenylstibide,²⁶³ selenide,²⁶⁴ telluride,²⁶⁴ and N,N-disubstituted amide enolate²⁶⁵ ions has been reported.

Singh et al.^{172,266} have proposed a mechanism similar to the aromatic $S_{RN}1$ mechanism, in the reactions of arenediazonium salts with various nucleophiles (Scheme I.22):

SCHEME I.22



Termination:



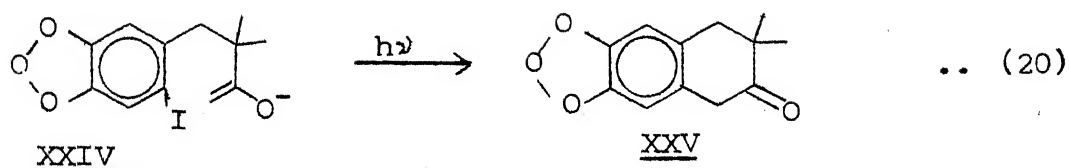
Nitro and hydroxy groups,^{244,249} apart from the nucleofugic group, interfere with aromatic $S_{RN}1$ processes. Steric hindrance has no noticeable effect on these reactions.²⁵⁰ Recently, Bunnett²⁶⁷ has shown that the nucleophilic reactivities differ in aromatic $S_{RN}1$ reactions by not more than a factor of 10. He has reasoned that this is due to combination of aryl radical with nucleophiles occurring at encounter-controlled rates.

There is no established example of the participation of an oxyanion nucleophile in an aromatic $S_{RN}1$ reaction to form an oxygen-arylated product. Bunnett²⁶⁷ has argued that the combination of an aryl radical with an oxyanion nucleophile would involve formation of a σ^* radical-anion at a very high energy level, a level inaccessible and thus the formation of a C-O bond in such a process is energetically not favourable.

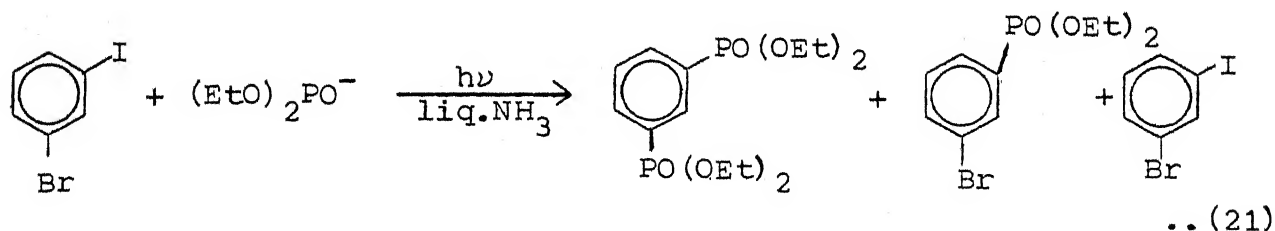
Several halogenated heterocyclic compounds including 2-, 3- and 4-halopyridines,^{243,249} 2-halopyrimidines,²⁶⁸ 2-chloropyrazine,^{243,268} 2-chloroquinoline,^{247,269,270} haloisoquinolines,^{258,271} halogen derivatives of thiophene,²⁷² 2-chloroquinoxaline,²⁷³ and 4-chloroquinoxaline²⁷³ are known to undergo $S_{RN}1$ reaction in the presence of suitable electron donors. Certain vinylic halides also undergo substitution via the $S_{RN}1$ pathway.²⁷⁴

Intramolecular $S_{RN}1$ reactions in substrates possessing appropriate structural features have been reported. Thus,

photostimulation of XXIV yields XXV in 99% yield²⁷⁵ (Eq. 20):

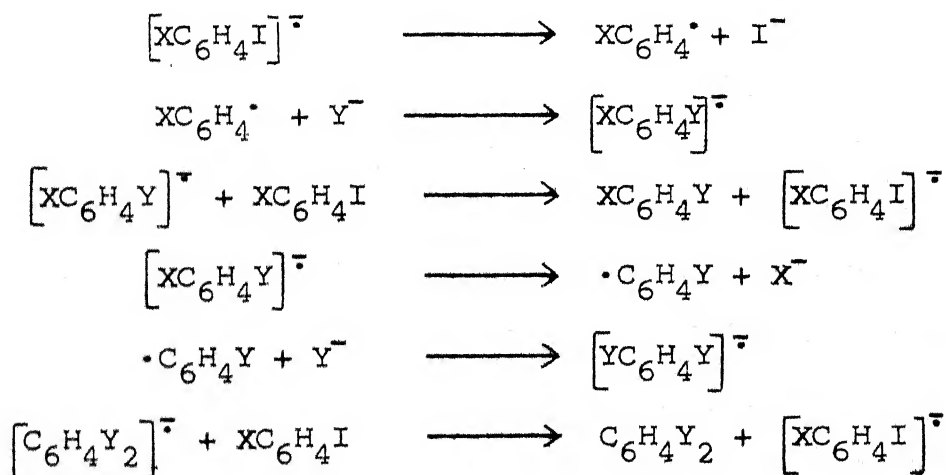


Reactions of dihalobenzenes with certain anions yield both the monosubstituted and disubstituted products.^{254, 255, 259, 276} Thus, irradiation of m-bromoiodobenzene with diethylphosphite ion in liquid NH_3 yields mostly the disubstituted product and a small amount of the monosubstituted product, along with unreacted starting material (Eq. 21):



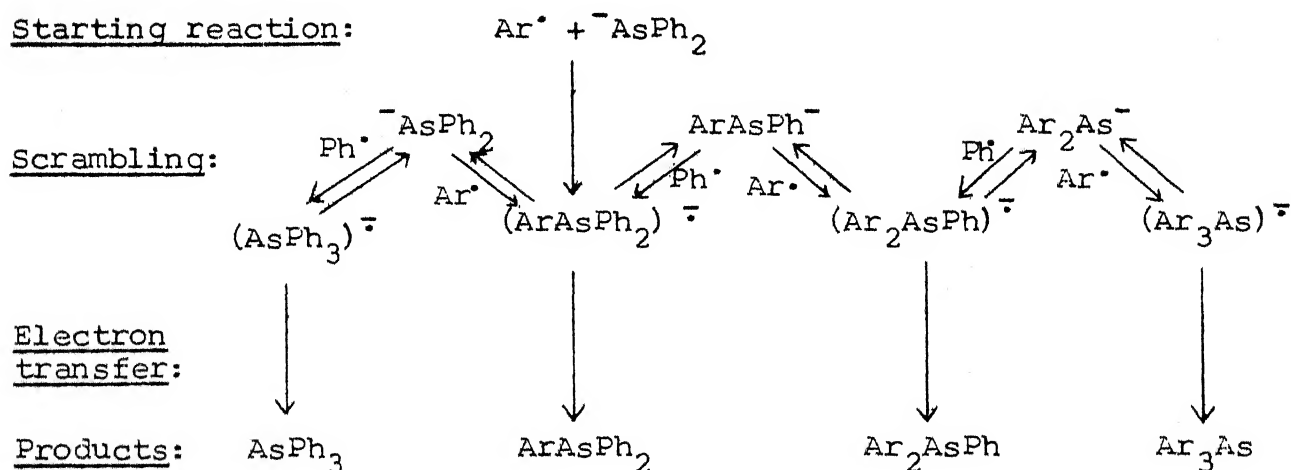
The $\text{S}_{\text{RN}}1$ mechanism presented in Scheme I.23 has been proposed to account for these observations:

SCHEME I.23



Recently, photostimulated reactions of haloaromatic compounds with potassium diphenylarsenide and potassium diphenylstibide in liquid NH_3 , have been reported.²⁶³ 1-Bromonaphthalene and 9-bromophenanthrene react with diphenylarsenide ion to give four arsines as products: triphenylarsine, diphenylarylarsine, phenyldiarylarisne and triarylarisne (aryl = 1-naphthyl, 9-phenanthryl). On the other hand, with 2-chloroquinoline as the substrate, only the straightforward substitution product 2-quinolyldiphenylarsine is formed. The mechanism suggested is outlined in Scheme I.24:

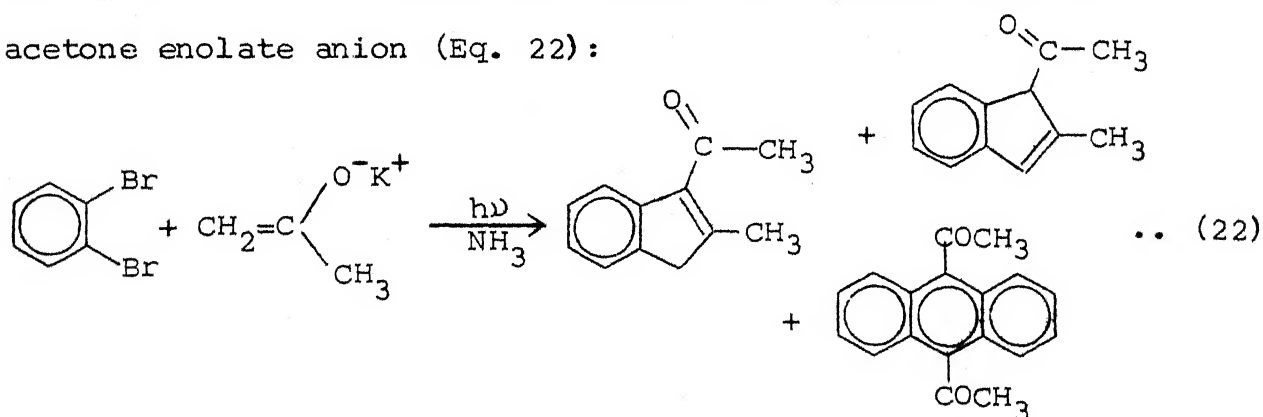
SCHEME I.24



Rossi et al.²⁶³ have suggested that in the process of coupling of an aryl radical with a nucleophile, σ and σ^* MO's are formed, and in case the σ^* MO's of the aryl-As bonds are the lowest energy MO's of the system, scrambling of aryl rings is observed. On the other hand if the π^* MO of the aryl moiety is lower in energy than the σ^* MOs of the aryl-As bonds,

as the aryl radical couples with the nucleophile, a σ^* MO is formed with the odd electron and by intramolecular electron transfer to the π^* MO, a π^* radical-anion is formed, and only the straightforward substitution product is obtained. Theoretical considerations confirm that the σ^* MO energy of the phenyl-As bond is lower than the π^* MO energy of naphthyl and phenanthryl moieties, thus leading to scrambling of aryl rings. On the other hand, the π^* MO energy of quinoline is lower than the σ^* MO energy of the phenyl-As bond, resulting in the straightforward substitution product.

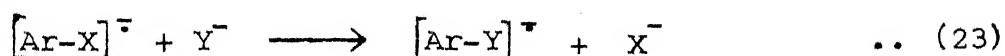
Aromatic $S_{RN}1$ reactions have been used to synthesize carbocyclic and heterocyclic ring systems. Synthesis of indoles,²⁷⁷ benzo-[b]-furanes²⁷⁸ and 2-azaindoles²⁷⁹ have been effected via the $S_{RN}1$ process. Recently, Bunnett and Singh²⁸⁰ have reported the synthesis of acetylmethylindenes from O-dibromobenzene and acetone enolate anion (Eq. 22):



Electrochemical method has also been used to initiate the $S_{RN}1$ mechanism leading to the synthesis of indoles from O-iodoaniline and acetone enolate anion.²⁸¹

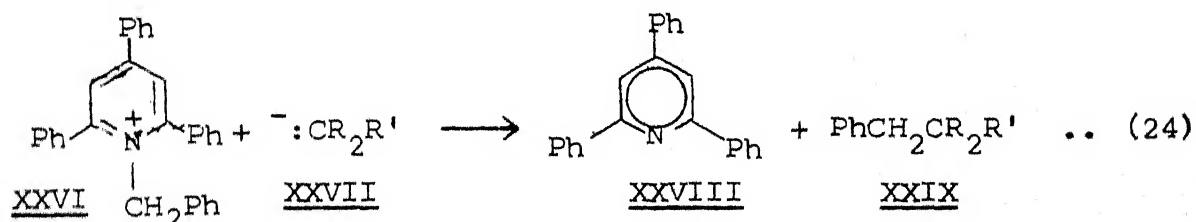
I.7 The S_{RN}2 Mechanism

An alternative mechanistic possibility to the propagation cycle of S_{RN}1 mechanism has been presented and dubbed S_{RN}2.^{253a} Its characteristic feature is that the nucleophile brings about direct displacement of the nucleofugal group from radical anion [Ar-X]^{•-} (Eq. 23):



According to this mechanism, the relative nucleophilic reactivity with various substrates, should depend on the leaving group. Bunnett et al.²⁶⁷ have presented evidence recently to show that the relative reactivity of two nucleophiles is independent of the leaving group in aryl halides. This is consistent with the S_{RN}1 mechanism but not with the S_{RN}2 mechanism.

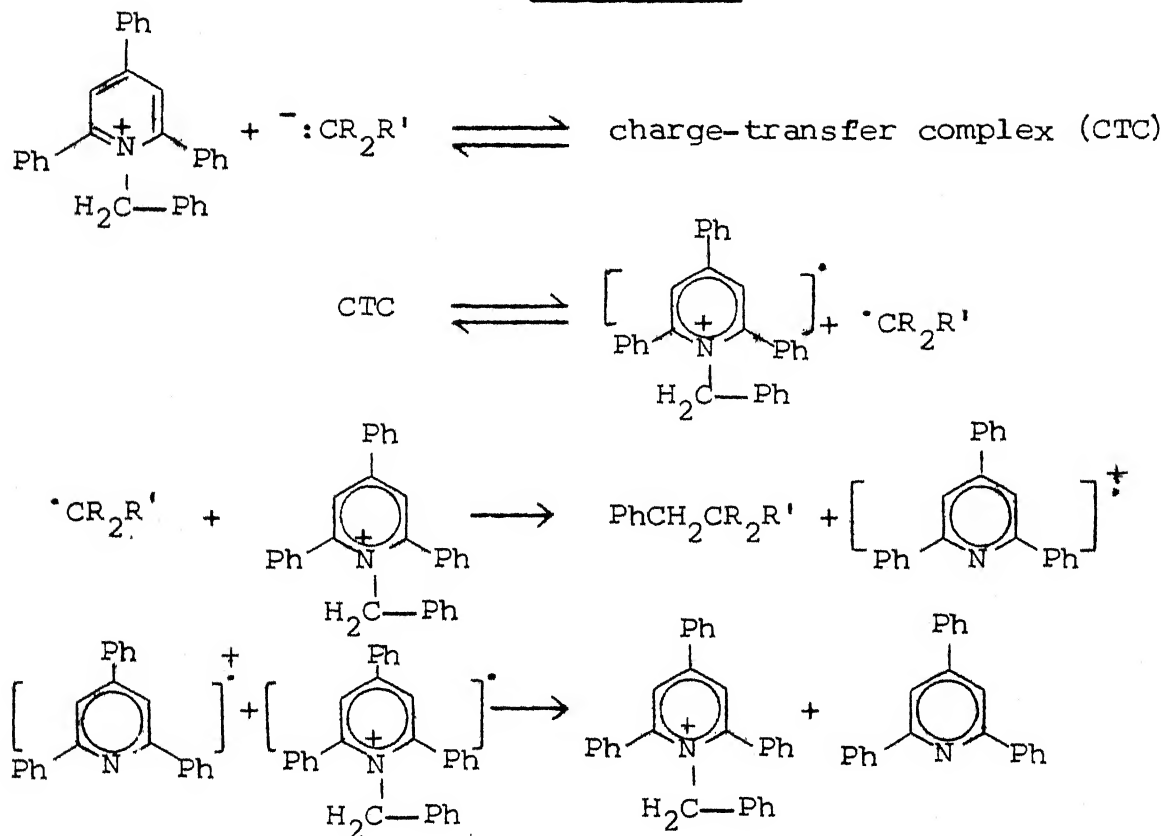
Recently, the symbol S_{RN}2 was applied rather confusingly, to a non-chain radical pathway proposed in the reaction of 1-alkylpyridinium cations XXVI with anions derived from nitroalkanes and ethylmalonate²⁸² (Eq. 24):



Katritzky and coworkers²⁸² have proposed the mechanism for these nucleophilic substitution reactions to occur via radical

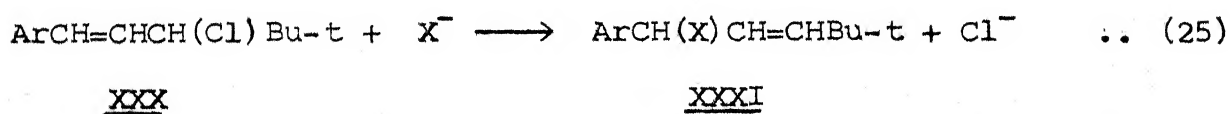
intermediates (Scheme I.25):

SCHEME I.25



I.8 The $\text{S}_{\text{RN}}1'$ Reaction - Radical Chain Substitution in Allylic Compounds

The first report of a radical-anion chain substitution reaction with allylic rearrangement is represented by the transformation of XXX to XXXI as shown in Eq. 25:

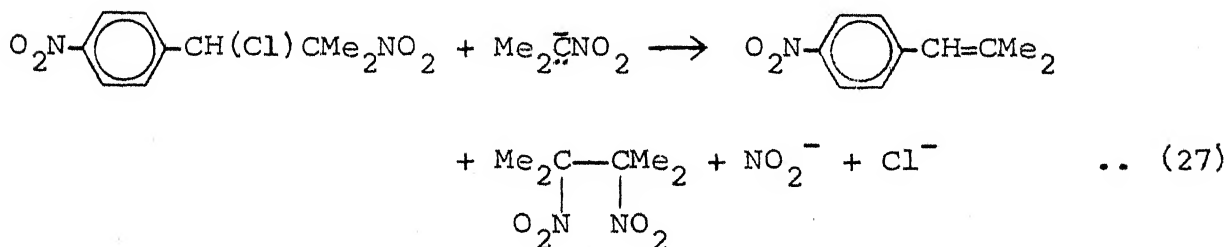
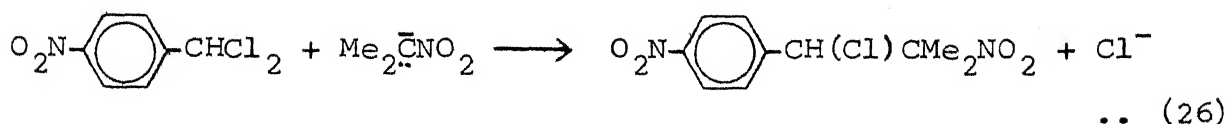


where $\text{Ar} = \text{p-O}_2\text{NC}_6\text{H}_4$ and $\text{X}^{\cdot-} = \text{Me}_2\text{C}^{\cdot-}\text{NO}_2$ or $\text{MeC}^{\cdot-}(\text{COOEt})_2$.

This corresponds to an $\text{S}_{\text{RN}}1'$ mechanism and has been named so by Norris and Barker.²⁸³

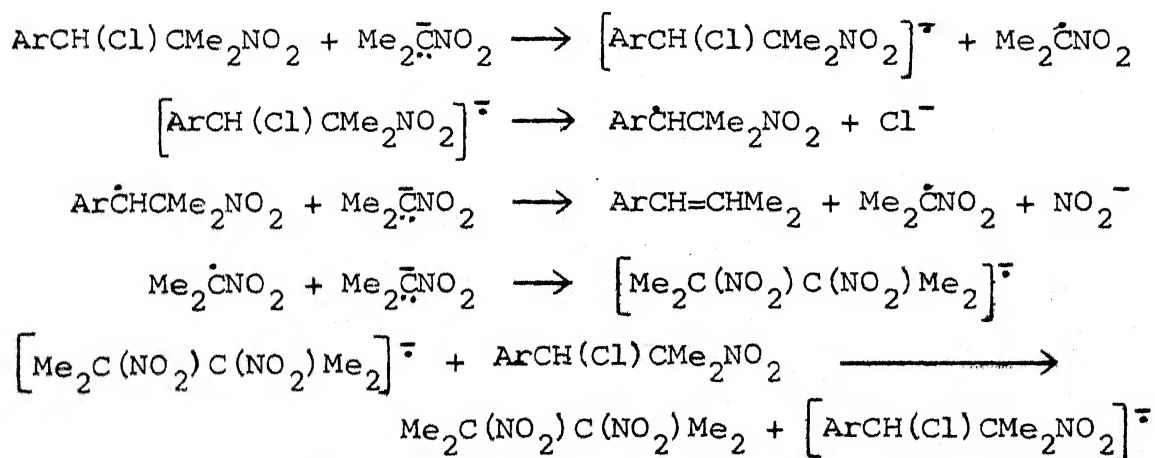
I.9 Elimination Reactions via Electron Transfer Processes

In recent years, it has been reported that certain elimination reactions of geminally and vicinally substituted leaving groups occur via electron transfer pathways. The reaction of p-nitrobenzylidene dichloride with 2-nitropropanate anion is postulated²⁸⁴⁻²⁸⁶ to be occurring in two steps as shown in Eqs. 26 and 27 :



Both the steps are inhibited by p-dinitrobenzene and accelerated by light. The first process is an $\text{S}_{\text{RN}}1$ reaction.⁸⁰ For the second process, Freeman and Norris²⁸⁴ have proposed the mechanism outlined in Scheme I.26:

SCHEME I.26

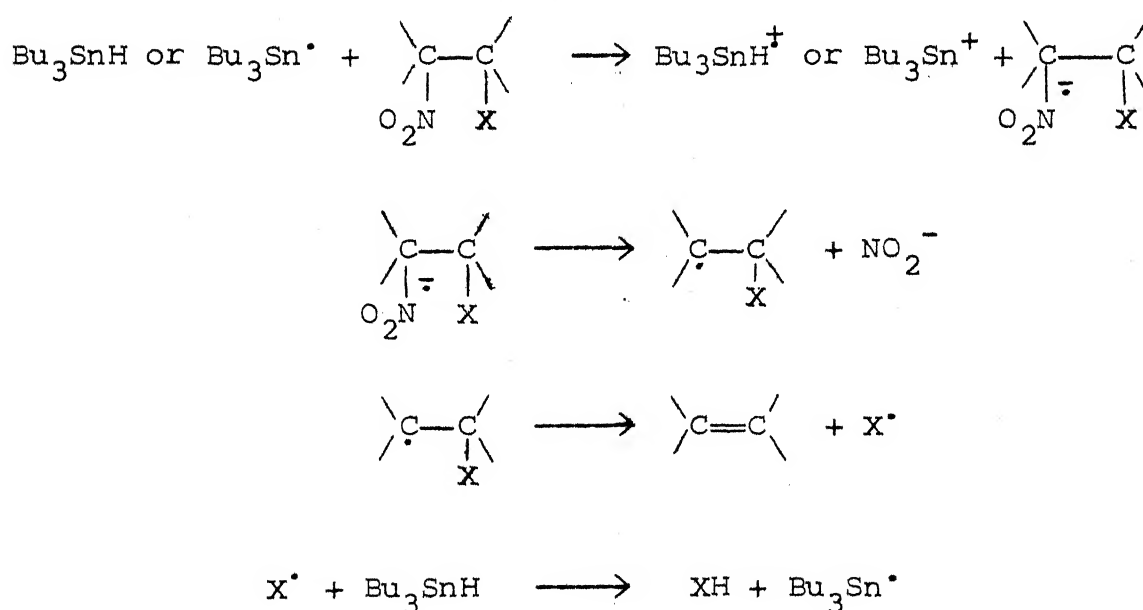


where $\text{Ar} = \text{O}_2\text{N}-\text{C}_6\text{H}_4-$

The above pathway has been named E_{RC1} (elimination, radical chain unimolecular) by Freeman and Norris.²⁸⁴

The conversion of vicinal dinitroalkanes into alkenes on treatment with either thiophenoxide or sulfide anions is also believed to occur by E_{RC1} mechanism.²²¹ Recently, E_{RC1} mechanism has been proposed in the conversion of vicinal dinitro or β -nitrosulfones with tributyltin hydride²⁸⁷ as shown in Scheme I.27:

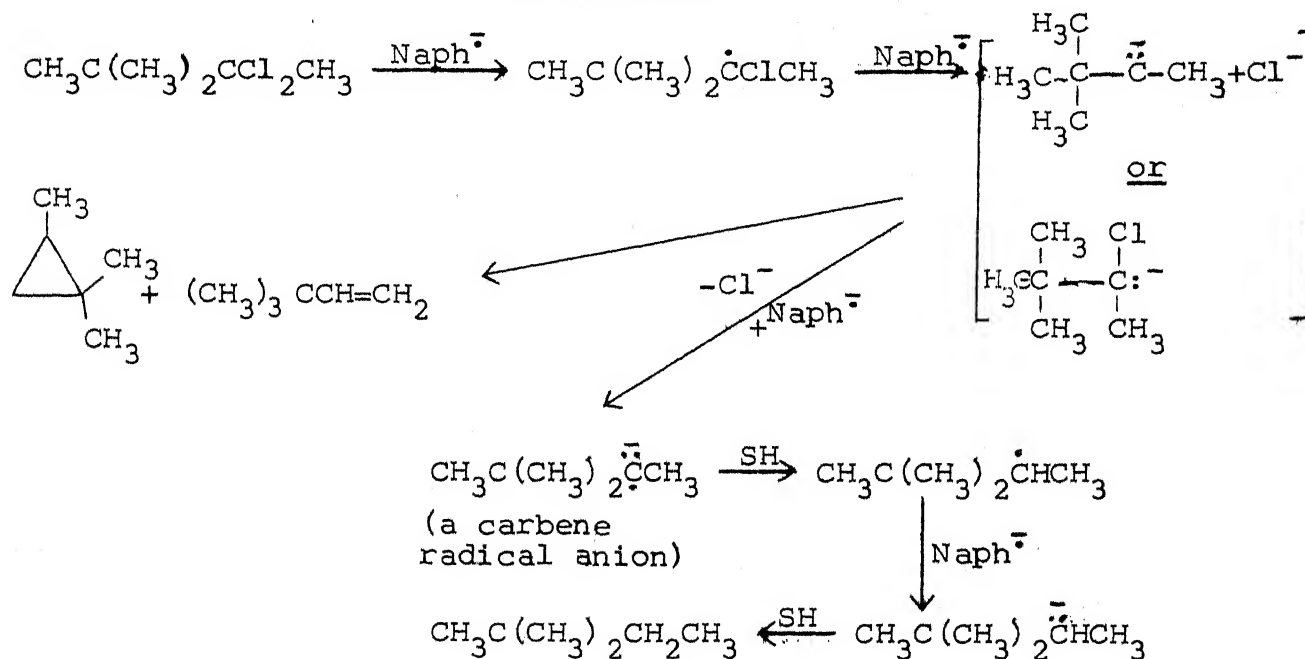
SCHEME I.27



Reductive elimination of cyclic phosphates,¹² cyano-hydrins,¹³ α -nitrosulfones²⁸⁸ and synchronous elimination of the nitro and ester groups or the nitro and keto groups in appropriate substrates²⁸⁹ have also been reported. Vicinal dihalides react readily with sodium naphthalene and disodium salt of phenanthrene giving olefins.^{290,291}

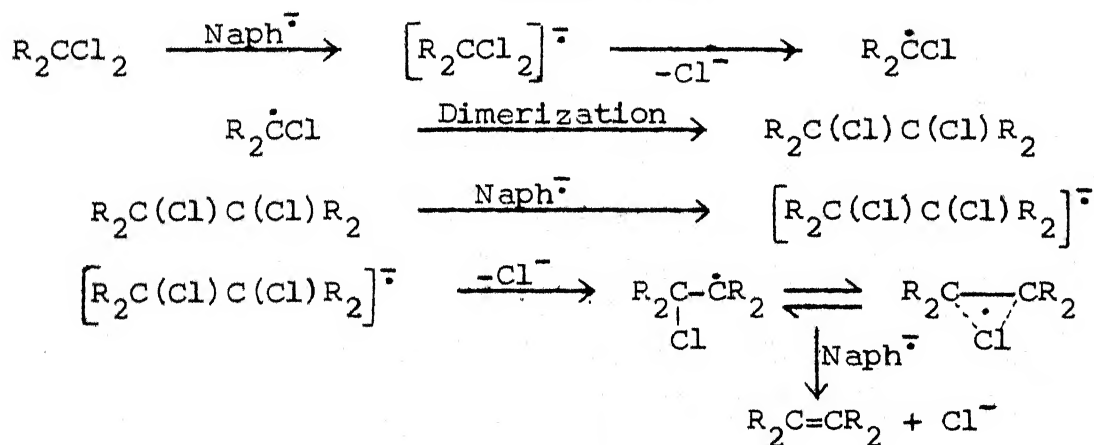
Sargent and coworkers²⁹² have proposed the existence of a new reactive intermediate called a carbene radical-anion in the reaction of 2,2-dichloro-3,3-dimethylbutane with sodium naphthalene. The proposed reaction pathway is summarized in Scheme I.28:

SCHEME I.28



Singh and Jayaraman²⁹³ have invoked the presence of bridged radicals in the reaction of gem-dichlorides with sodium naphthalene as shown in Scheme I.29:

SCHEME I.29



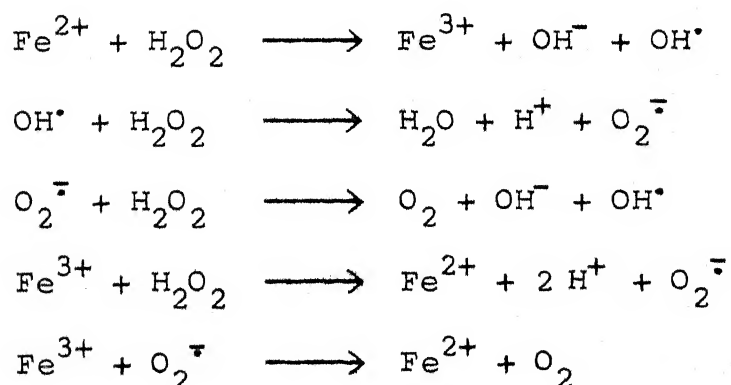
Base catalyzed elimination reactions of 4-nitrobenzyl halides and dimethyl-4-nitrobenzylsulfonium ion,^{294,295} have been reported to occur via electron transfer pathways.

I.10 Electron-Transfer in Bio-Processes

Electron transfer processes, leading to the formation of free radicals, have been reported to occur in several important biological systems. Though a complete discussion of such processes is out of the scope of this chapter, a few important examples are described to highlight the significance of such processes.

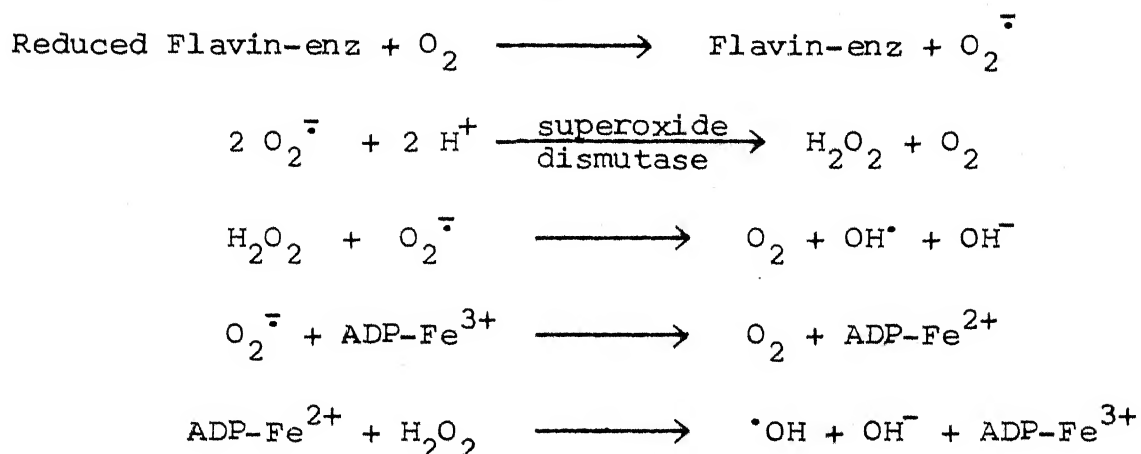
Transition metal complexes, which occur in the cell, catalyze the decomposition of peroxides.²⁹⁶⁻²⁹⁹ The process is thought to be similar³⁰⁰ to the well known Haber-Weiss cycle³⁰¹ in which iron catalyzes the decomposition of H_2O_2 by an electron transfer pathway, leading to the formation of hydroxyl radicals, as shown in Scheme I.30:

SCHEME I.30



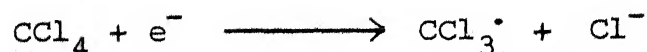
McCay et al.^{302,303} have pointed out that several oxidative enzymes, such as xanthine oxidase, also produce hydroxyl radicals by a sequence of reactions involving superoxide ion and hydrogen peroxide in presence of chelated iron, as shown in Scheme I.31:

SCHEME I.31



Hydroxyl radicals so formed are potent oxidants and may initiate chain reactions in the surrounding lipid membranes leading to the destruction of tissues and consequently to aging.³⁰⁴

The toxicity in small doses of chloro compounds, such as chloroform and CCl_4 , has been suggested to be due to the peroxidation of endoplasmic reticulum lipids in a reaction initiated by an electron transfer from electron donors or donor sites in enzymes^{305,306} (Eq. 28):

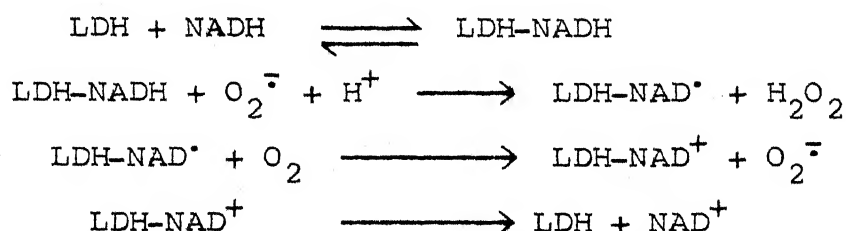


Ethanol, even in small doses, may induce a radical chain reaction in the liver mitochondrial lipids possibly leading to fat accumulation and necrosis typical of alcoholism. In this case

too, the initial radical production may result by an electron transfer from an intermediate in the normal electron transport chain.³⁰⁷

One electron transfer also occurs in some systems in the propagation steps. A study of the superoxide-NADH system has revealed that the oxidation of NADH in presence of an enzyme lactate dehydrogenase is a chain reaction for which the mechanism shown in Scheme I.32 has been suggested:^{308, 309}

SCHEME I.32



Photosynthetic reactions are known to occur mostly by one electron transfer processes.³¹⁰ This represents a clear case in which free radical biology plays an important role in the processes of interest and relevance to man.

The foregoing discussion highlights the significance of electron transfer processes in chemical and biological systems and reveals that though much ground has been covered in this area, a lot still remains unexplored and thus offers challenging opportunities for mechanistic investigations. In view of this, we decided to study a few reactions, described in the following chapters, which were known to proceed by uncertain pathways and have now been found by us to involve electron transfer processes.

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CHAPTER II

SIMULTANEOUS OCCURRENCE OF ELECTRON
TRANSFER INITIATED RADICAL CAGE
COLLAPSE AND CHAIN MECHANISMS IN THE
REACTIONS OF DIARYLIODONIUM CATIONS
WITH 2-NITROPROPANATE ANION

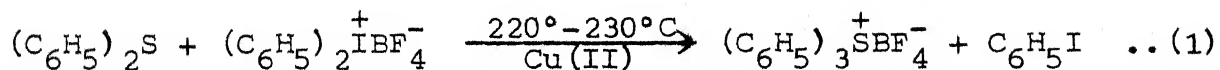
II.1 Abstract

Intervention of radicals in the reactions of arenediazonium salts with certain anions as reported earlier has been satisfactorily explained in terms of single electron transfer pathways; but the mode of initiation and bond reorganization in the free radical reactions of diaryliodonium salts with anions is poorly understood in the existing literature. A study of the reactions of diphenyliodonium bromide, phenyl-p-tolyliodonium bromide and phenyl-p-anisyllyliodonium bromide with lithium 2-nitropropan-2-ide has been carried out in methanol medium at 30°C,

under varying conditions. The formation of arylated nitroparaffins on one hand and benzene, toluene, anisole, biaryls and formaldehyde on the other, in these reactions has been found to occur by two competing pathways involving free radical intermediates. Our observations clearly eliminate the possibility of occurrence of an S_NAr process and the intervention of aryne intermediates, in these reactions. These reactions were catalyzed by light and inhibited in the presence of oxygen. Simultaneous occurrence of free radical cage and chain mechanisms initiated by single electron transfer from the 2-nitropropanate anion to the diaryliodonium cation, has been proposed which satisfactorily accounts for the observed experimental facts.

II.2 Introduction

Diaryliodonium salts are recognized as versatile arylating agents. Arylation of several anions¹⁻⁴ including carbanions⁵⁻¹⁰ has been achieved by means of reactions with diaryliodonium cations. A new preparation of triarylsulfonium and selenonium salts has been reported¹¹ via the Cu(II) catalysed arylation of sulfides and selenides with diaryliodonium salts (Eq. 1):

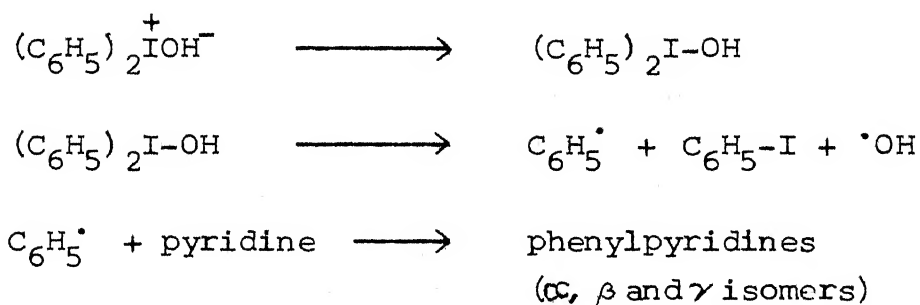


Mechanisms presented for the phenylation of anions with diaryliodonium cations include nucleophilic substitution,^{1-3, 12, 13} as well as the formation and subsequent reactions of various

intermediates like a phenyl cation,¹ diaryliodonine,^{4,14,15} a trisubstituted iodine¹⁶ and an aryne.^{13,17}

Several reactions of iodonium salts have been discussed in terms of free radical intermediates. Sandin and Brown¹⁸ have postulated the formation and decomposition into radicals, of a trisubstituted iodine, in the reaction of diphenyliodonium chloride with sodium hydroxide in the presence of pyridine (Scheme II.1):

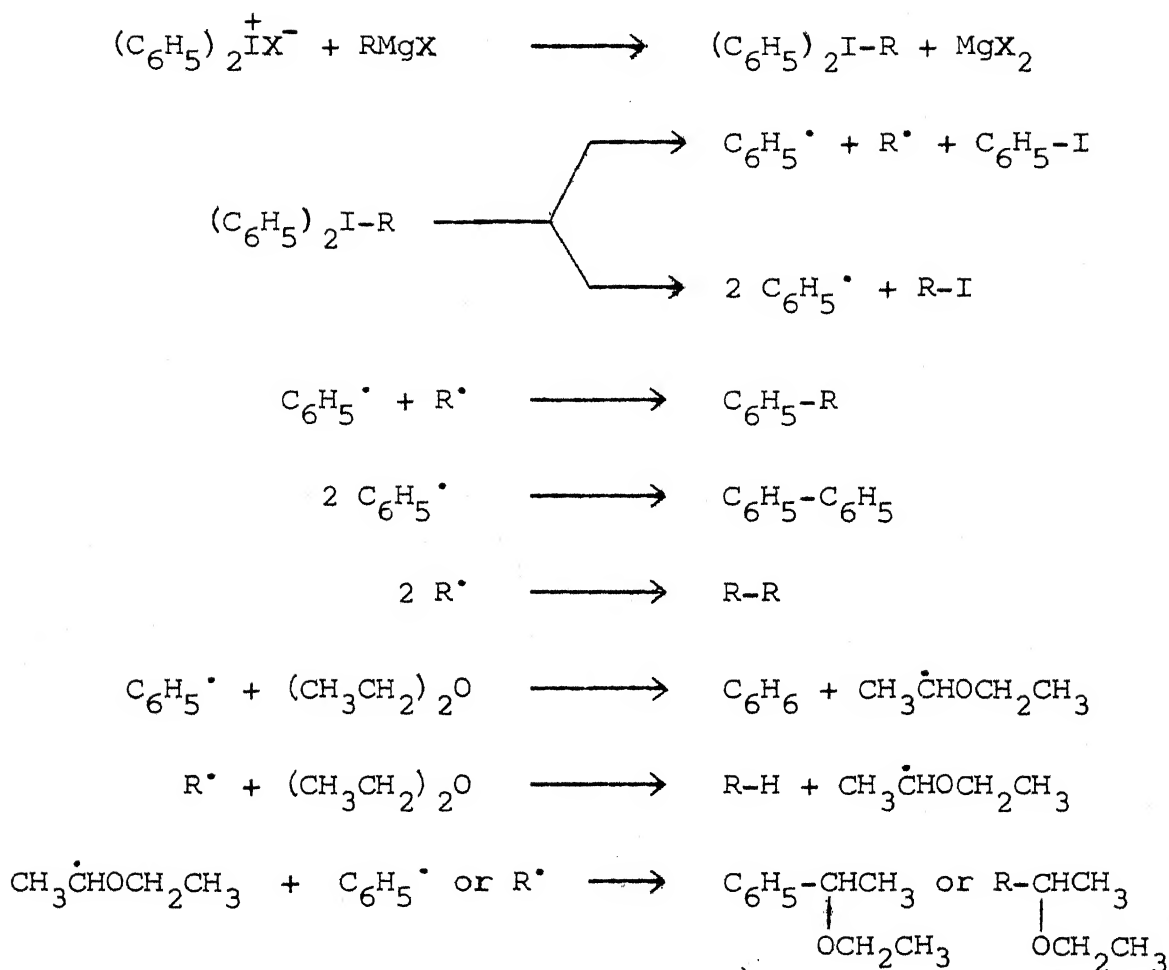
SCHEME II.1



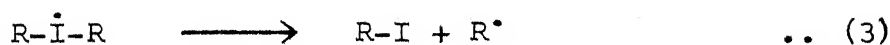
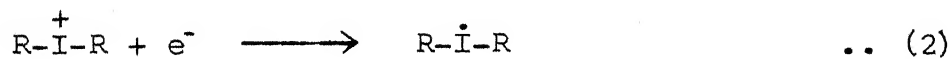
A similar mechanism has been proposed for the hydrolysis of iodonium salts.¹⁷

Reactions of organolithiums and organomagnesium halides with diaryliodonium salts have been investigated by Beringer and coworkers.¹⁶ They have provided evidence for the formation of a trisubstituted iodine, which decomposes to yield aryl-iodides and free radicals, which react further to yield the products shown in Scheme II.2.

Polarographic and Coulometric studies¹⁴ of iodonium salts have revealed that diaryliodonium cation may accept an electron forming diaryliodonine, which being unstable, rapidly decomposes

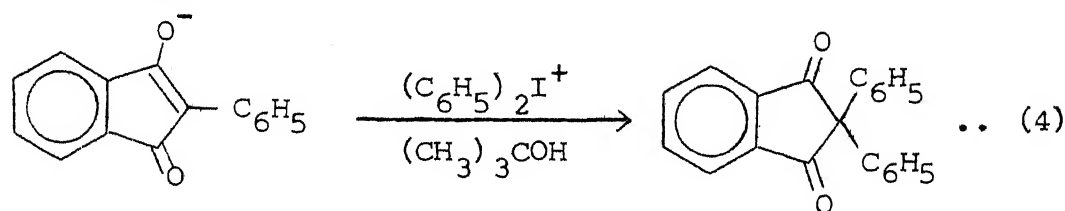
SCHEME II.2

to give aryl iodide and an aryl free radical (Eqs. 2 and 3):



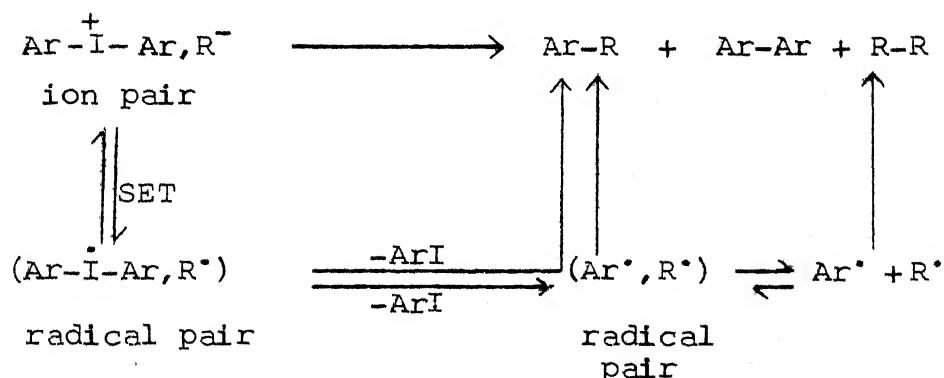
The half wave potentials of substituted iodonium salts are not strongly affected by the nature of the substituent in the benzene ring.¹⁹

The anions of dimedone,⁶ di- and tribenzoylmethanes,⁶ 1,3-indandiones,^{7,10} esters^{8,9} and dianions of β -diketones²⁰ have been arylated with diaryliodonium cations. In tert.butyl-alcohol medium, the reaction of 2-phenyl-1,3-indandione anion with diphenyliodonium chloride, yields 85% 2,2-diphenyl-1,3-indandione⁷ (Eq. 4):



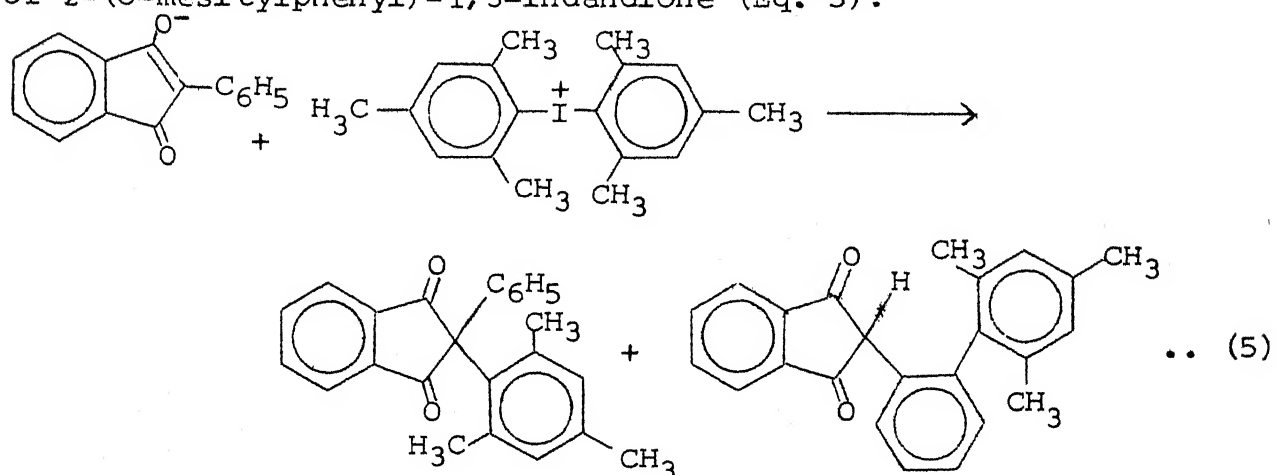
This reaction also yields small amounts of hydrocarbons and biaryls. It is inhibited in the presence of oxygen and styrene. Based on these facts, an electron transfer cage collapse mechanism, shown in Scheme II.3, has been proposed:⁷

SCHEME II.3



The 2-phenyl-1,3-indandione-2-yl free radical couples with phenyl free radical almost exclusively through the 2-position, presumably because C,C-coupling has a lower energy of activation than O,C-coupling. If, however, either of these phenyl groups is enlarged to a bulkier mesityl group, the coupling through

the 2-position is substantially slowed down while the rate of diffusion out of the cage of radicals remains essentially unchanged. This results in the formation of larger amounts of cage escape products.¹⁰ Thus, the anion of 2-phenyl-1,3-indandione with dimesityliodonium chloride yields only 23% of the analogous 2-mesityl-2-phenyl-1,3-indandione and a small amount of 2-(o-mesitylphenyl)-1,3-indandione (Eq. 5):

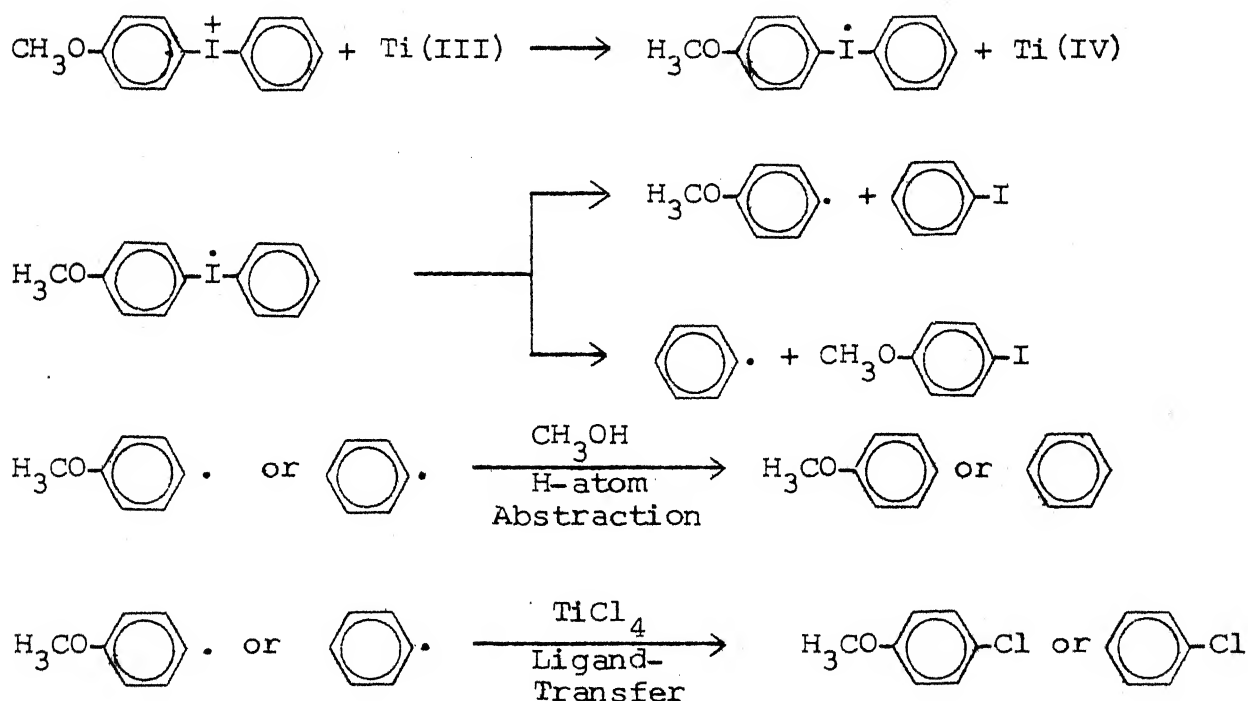


To analyze the mechanism of the reaction of diaryliodonium ions with nucleophiles and reductants, Beringer and Falk²¹ have examined the reactions of various p-substituted and p,p'-disubstituted diphenyliodonium salts with several anions including carbanions. They have observed that the presence of a p-nitro group enhances and that of a p-methoxy group depresses the susceptibility of diphenyliodonium ion towards nucleophilic attack. Among the anions used for the study, carbanions react predominantly by an electron transfer mechanism, whereas certain inorganic anions e.g. sulfite ion, react by a nucleophilic S_NAr mechanism.

Salts of Ti(III), Cr(II) and Cu(I) have been used for the chemical reduction of diaryliodonium salts.²² Thus, the reduction

of phenyl-p-anisylidodonium cation with Ti(III), in methanol solvent, yields hydrocarbons as the major product. On the other hand, the reaction in presence of large amounts of TiCl_4 , in aqueous medium, yields chlorobenzene and p-chloroanisole as major products. The mechanism suggested for these reactions involves ligand transfer from TiCl_4 subsequent to an electron transfer from Ti(III) as shown in Scheme II.4:

SCHEME II.4



The ratio of cleavage products $\text{p-CH}_3\text{O-C}_6\text{H}_4\text{-I/C}_6\text{H}_5\text{-I}$ is ca. 0.7 reflecting that the cleavage of aryl-I bond is not much affected by the presence of a p-methoxy group in one of the aryl rings.

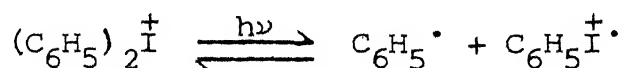
Reutov and coworkers^{15,23} have demonstrated the formation of a hypervalent iodine intermediate in the $\text{S}_\text{N}\text{Ar}$ reactions of

diaryliodonium cations with aromatic amines. They have also shown that the corresponding reactions with aliphatic amines²⁴ and triphenylphosphine²⁵ have an important mechanistic component where radicals intervene.

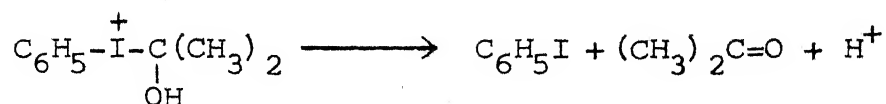
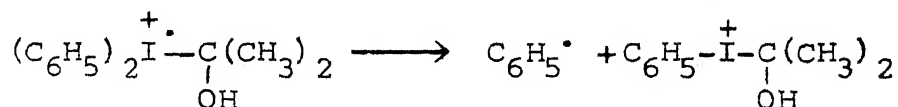
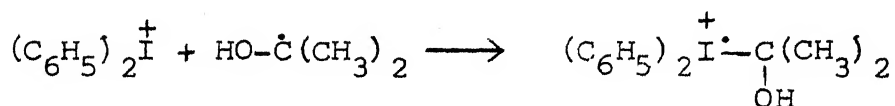
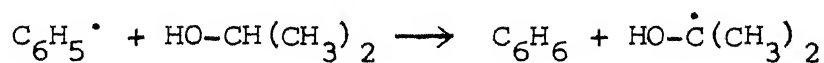
Photolysis of diphenyliodonium salts in isopropyl alcohol has also been reported²⁶ to proceed through a radical chain mechanism shown in Scheme II.5:

SCHEME II.5

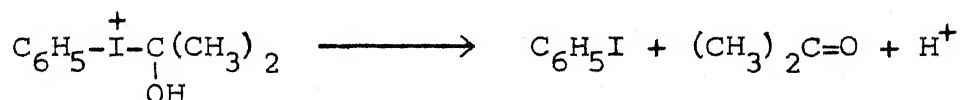
Initiation:



Propagation:



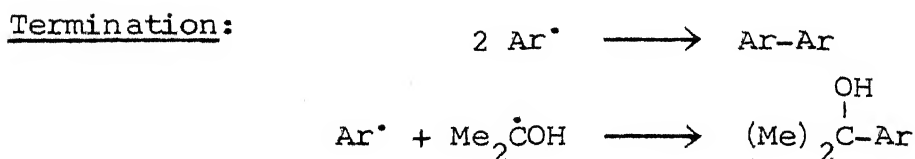
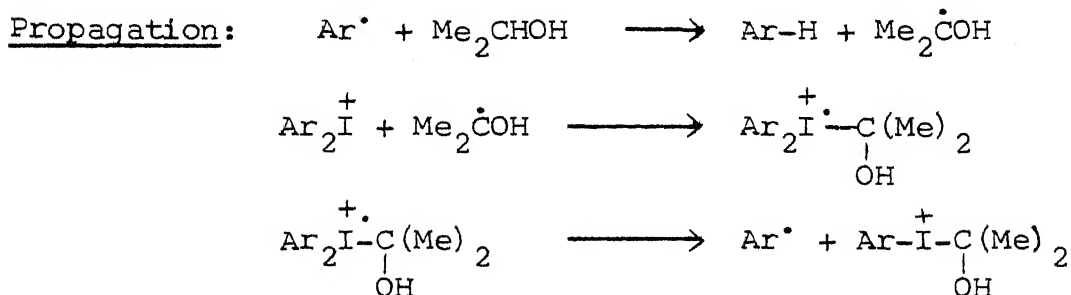
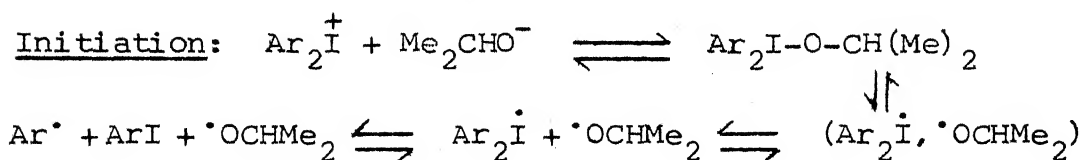
Termination:



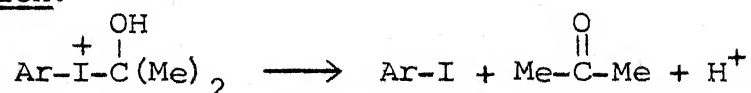
These photolytic reactions are inhibited in the presence of a small amount of 1,1-diphenylethylene, thus establishing the radical nature of the mechanism.

The reactions of diaryliodonium salts with a metal alkoxide to give alkylaryl ethers and aryl iodides are considered to be of synthetic utility. However, it has been reported²⁷ that aromatic hydrocarbons, aryl iodides and an aldol resin are frequently the major products. McEwen and coworkers²⁸ have postulated that the former products arise by an aromatic nucleophilic displacement reaction, while the latter products result from a radical chain mechanism shown in Scheme II.6:

SCHEME II.6



Subsequent reaction:

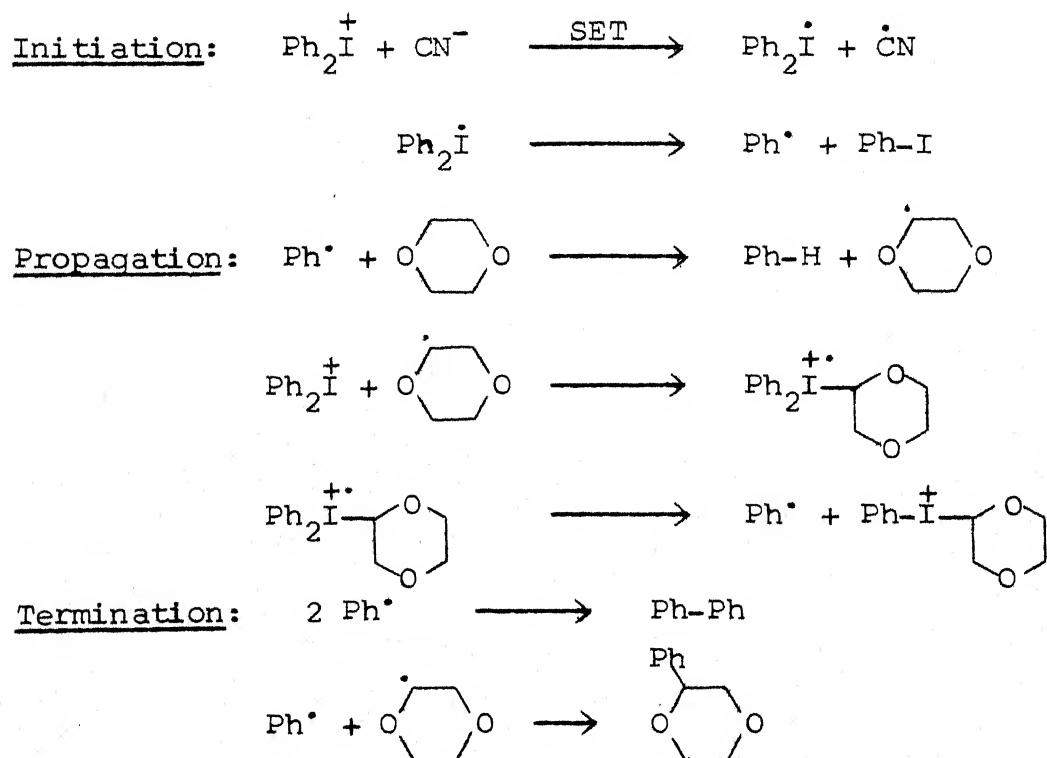


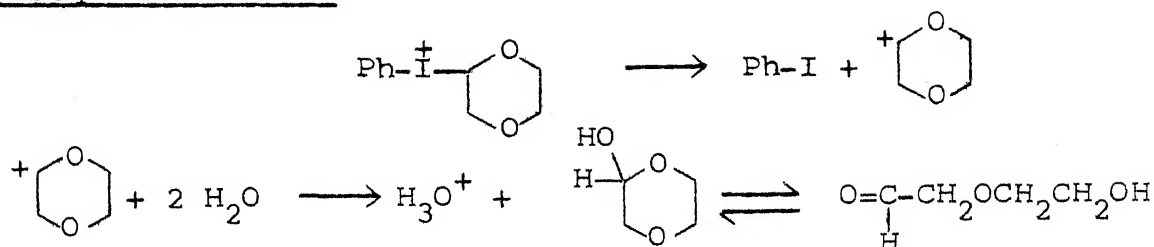
Recently, departure aptitudes of various aryl radicals from trisubstituted radical cations have been calculated from

quantitative determination of products, in the reactions of several unsymmetrical diaryliodonium fluoroborates with sodium ethoxide.²⁹ The observed values of departure aptitudes have been found to be consistent with values obtained from the Hammett plot for the iodonium salt reaction and the polar substituent constant σ^* values for various substituents.

Aromatic hydrocarbons obtained in the reactions of diaryliodonium fluoroborates with nitrite, azide and thiocyanate anions have also been shown³⁰ to arise via a radical chain mechanism, similar to the one shown in Scheme II.6. The initiation step of the radical chain mechanism in the reaction of diphenyliodonium ion with cyanide ion probably involves a single electron transfer process. The mechanism proposed³⁰ for this reaction in dioxane medium is shown in Scheme II.7:

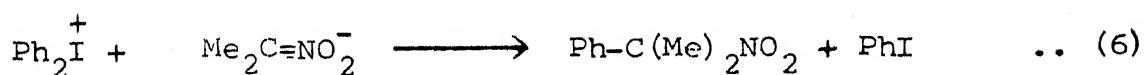
SCHEME II.7



Scheme II.7 (contd.)Subsequent reaction:

Based on the ratio of the arylated products obtained in the reaction of phenyl-p-tolyliodonium fluoroborate with cyanide ion, an $\text{S}_{\text{N}}\text{Ar}$ mechanism has been proposed for the formation of arylcyanides in these reactions.

The reaction of 2-nitropropan-2-ide ion with diphenyliodonium tosylate, in DMF solvent, has been reported³¹ to give 56% yield of 2-phenyl-2-nitropropane; but no mechanistic inferences have been drawn in this report (Eq. 6):

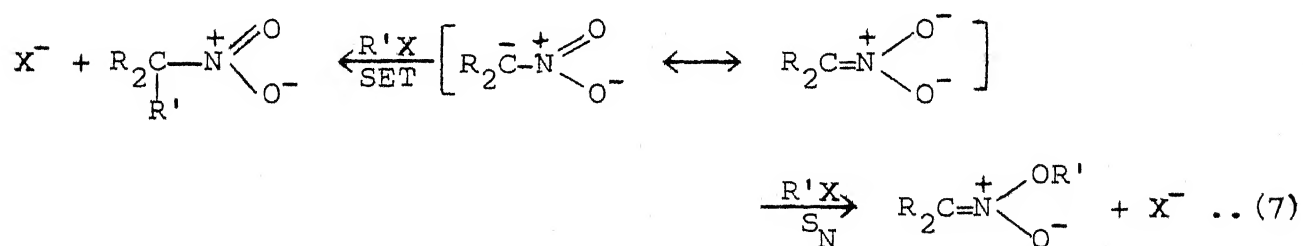


In view of the immense synthetic utility of diaryliodonium salts as arylating agents and diverse mechanistic possibilities involved in their reactions, we decided to investigate the mechanistic details of the reactions of a few diaryliodonium salts with 2-nitropropanate anion.

II.3 Results and Discussion

The reactions of diaryliodonium salts with certain anions, especially carbanions are known to proceed via the intervention of free radicals, but the mode of initiation³⁰ and bond reorganization²¹ in these reactions is poorly understood. The reaction of 2-nitropropanate anion with diphenyliodonium tosylate, in DMF solvent, has been reported³¹ to yield 56% of 2-phenyl-2-nitropropane, but no mechanistic inference has been drawn in this report.

The ambident 2-nitropropanate anion is known to react with appropriate substrates by donating an electron³²⁻³⁴ or by a nucleophilic process.³⁵ Thus, it may be used as a probe for investigating the mechanistic details of the reactions in which it participates (Eq. 7):



The present study was undertaken with a view to establishing the mechanisms operative in the reactions of diaryliodonium cations with the ambident 2-nitropropanate anion. Simultaneous occurrence of electron transfer initiated radical cage and chain mechanisms have been demonstrated by us, in the reactions of three diaryliodonium cations, viz., diphenyliodonium cation $\text{Ph}-\text{I}^+-\text{Ph}$ Ia,

TABLE II.1: Reactions^a of Diaryliodonium bromides with Lithium-2-Nitropropan-2-ide in Methanol at 30°C

Run	Diaryl- iodonium bromide I	Reaction Atmos- phere	Time (hr)	% Yield of Products ^b										Starting Material I/e
				Ph-H	Ar-H	PhCMe ₂ NO ₂	ArCMe ₂ NO ₂	Ph-I	Ar-I	Diaryls	O ₂ NMe ₂ C- O ₂ NMe ₂ C	CH ₂ OP		
1	Ia	Nitrogen	48	43	-	41	-	94	-	5	5	38	-	
2	Ia	Oxygen ^f	96	5	-	6	-	18	-	-	-	-	80	
3 ^g	Ia	Nitrogen	48	38	-	22	-	70	-	3	2	32	30	
4 ^h	Ia	Nitrogen	48	8	-	67	-	88	-	2	2	-	10	
5 ⁱ	Ia	Nitrogen	48	38	-	36	-	87	-	4	4	33	10	
6	Ib	Nitrogen	48	23	21	24	16	44	54	5 ^j	6	37	-	
7	Ib	Oxygen ^f	96	4	4	3	2	8	10	-	-	-	80	
8 ⁱ	Ib	Nitrogen	48	20	18	21	14	38	47	4 ^j	5	32	12	
9	Ic	Nitrogen	48	23	18	28	13	38	57	6 ^k	5	35	-	
10	Ic	Oxygen ^f	96	4	4	2	2	6	8	-	-	-	85	
11 ⁱ	Ic	Nitrogen	48	18	15	25	11	33	50	4 ^k	5	30	15	

a, Unless otherwise stated, 5 x 10⁻³ mol of diaryliodonium bromide was reacted

...contd.

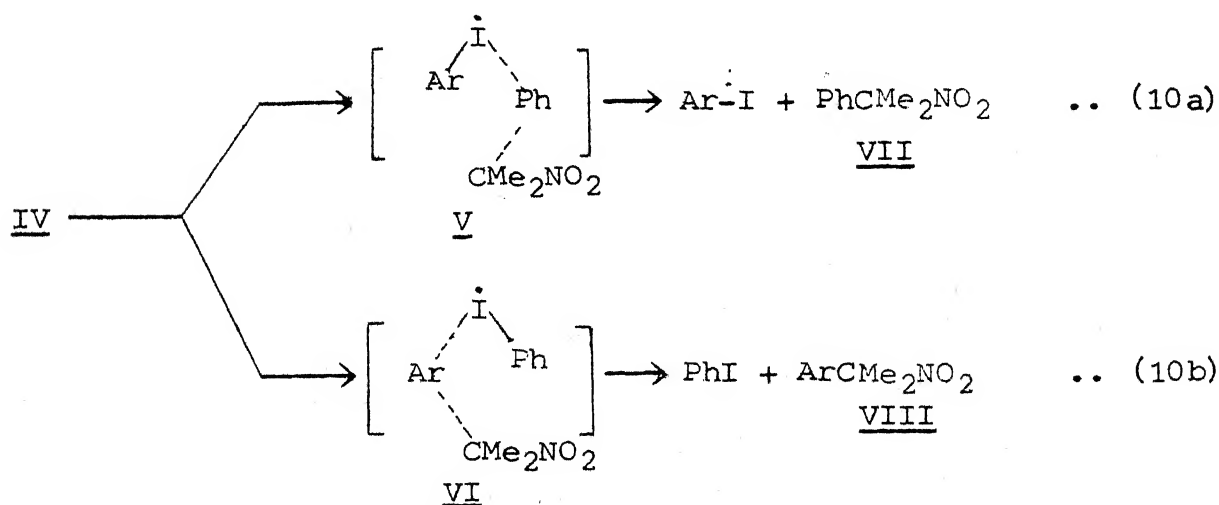
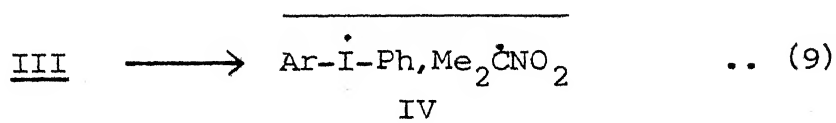
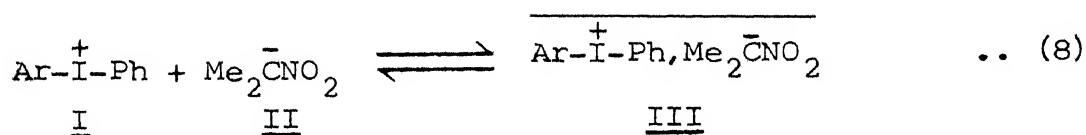
Table II.1 (contd.)

- with lithium 2-nitropropan-2-ide (0.01 mol) under laboratory lights.
 $\text{Ia} = \text{C}_6\text{H}_5-\overset{+}{\text{I}}-\text{C}_6\text{H}_5\text{Br}^-$; $\text{Ib} = \text{p-CH}_3-\text{C}_6\text{H}_4-\overset{+}{\text{I}}-\text{C}_6\text{H}_5\text{Br}^-$; $\text{Ic} = \text{p-CH}_3\text{O-C}_6\text{H}_4-\overset{+}{\text{I}}-\text{C}_6\text{H}_5\text{Br}^-$.
- b, Percentages based on diaryliodonium bromide unless otherwise stated; phenol 9%, 4% and 5% was also obtained in runs 2, 7 and 10, respectively, besides p-cresol 4% in run 7 and p-methoxyphenol 4% in run 10.
- c, Percentages based on lithium 2-nitropropan-2-ide.
- d, Estimated as dimedone derivative.
- e, Recovered and estimated as diaryliodonium iodide.
- f, Oxygen was bubbled through the reaction mixture.
- g, With 5×10^{-3} mol of lithium 2-nitropropan-2-ide.
- h, In presence of α -methylstyrene (0.01 mol);
- i, In dark.
- j, Biphenyl 3%, di-p-tolyl 2% in run 6 and biphenyl 2%, di-p-tolyl 2% in run 8, with traces of p-methylbiphenyl.
- k, Biphenyl 3% and di-p-anisyl 3% in run 9 and biphenyl 2%, di-p-anisyl 2% in run 11, with traces of p-methoxybiphenyl.

The S_NAr mechanism envisaged with the staggered pyramidalized conformation of the nucleophile $\bar{C}(\text{CH}_3)_2\text{NO}_2$, leading to C-arylation only, has a low probability of occurrence due to the high energy (+43 kcal/mol) of this conformation.³⁶ Furthermore, the formation of arylated nitroparaffins by an S_NAr mechanism is also ruled out due to the fact that the ratio of 2-phenyl-2-nitropropane : 2-(p-tolyl)-2-nitropropane formed in the reaction of phenyl-p-tolyliodonium bromide (run 6) is 1.67. This value is much less than expected in an S_NAr process, since 2-nitrobromobenzene is known to undergo an aromatic nucleophilic substitution reaction with piperidine about 7 times faster than does 2-nitro-4-methylbromobenzene.³⁷ Also, in other known³⁸ nucleophilic reactions with diaryliodonium salts the ratio of the cleavage of Ph-I bond to p-Me-C₆H₄-I bond in Ph-I⁺-C₆H₄-Me-p is more than twice the value obtained in run 6. Our inability to detect any 2-(m-tolyl)-2-nitropropane or 2-(m-anisyl)-2-nitropropane among the products in the reactions of phenyl-p-tolyliodonium bromide and phenyl-p-anisyliodonium bromide, respectively, inspite of careful search clearly eliminates the possibility of aryne intermediates in the reactions under study. These reactions are sensitive to photochemical catalysis as evident from the observed retardation in the absence of light (runs 5, 8 and 11). These arguments coupled with the observed inhibition in the presence of oxygen (runs 2, 7 and 10), indicate effective intervention of radicals in these reactions.

In view of the known²² function of diaryliodonium cations as electron acceptors under suitable conditions and that of the 2-nitropropanate anion as an electron donor towards comparatively weak acceptors,³⁹ we propose that the electron transfer process outlined in Scheme II.8, accounts for the formation of major portions of arylated nitroparaffins VII and VIII in addition to iodoarenes.

SCHEME II.8



The proposed pathway suggests that on mixing the two reactants, the nitropropanate anion associates with the diaryliodonium cation to form an ion pair III in a reversible reaction. The reversibility of the first step of Scheme II.8 (Eqn. 8)

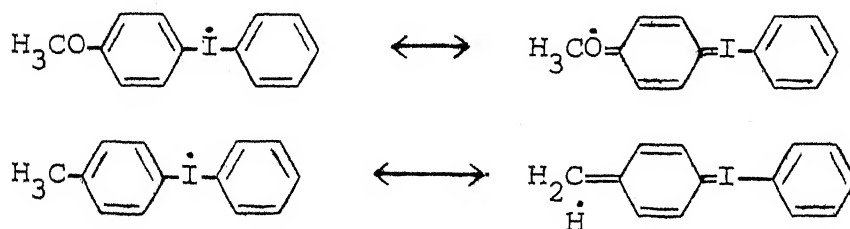
is established by the fact that increasing amounts of 2-nitropropanate anion result in enhanced yields of the products derived from the ion pair III i.e. arylated nitroparaffins. The 2-nitropropanate anion then transfers an electron to the diaryliodonium cation, resulting in the radical pair IV. The decomposition of this radical pair IV, in the solvent cage, then yields the arylated nitroparaffins VII and VIII. The product ratios in similar radical reactions of diaryliodonium salts with different anions are dependent on the nature of the reducing anion.²¹ Thus, transition states resembling V and VI could be visualized for the formation of 2-phenyl-2-nitropropane VII and 2-aryl-2-nitropropane (2-(p-tolyl)-2-nitropropane or 2-(p-anisyl)-2-nitropropane) VIII, respectively.

The development of a low energy transition state would be favoured by the lengthening of the energetically weaker C-I bond during the homolysis of $p\text{-R-C}_6\text{H}_4\text{-}\dot{\text{I}}\text{-Ph}$, as well as on the stabilities of the transition states V and VI. Since the value of ρ in Hammett correlations of departure aptitudes of aryl groups in such radical dissociations is positive, the bond dissociation energy (BDE) of the aryl carbon-I bonds would follow the order: $\text{Ph} < p\text{-Me-C}_6\text{H}_4 < p\text{-MeO-C}_6\text{H}_4$.²⁹ Furthermore, though in the unsubstituted diphenyliodonium cation, resonance interaction in which iodine expands its valence shell to accommodate electrons in its 5d orbital is negligibly small, it is established that such an interaction may become significant in the electronic excited state by the presence of

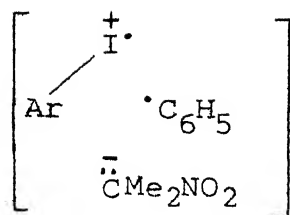
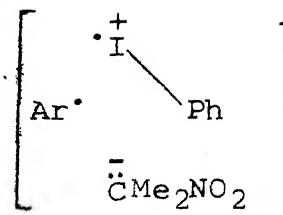
electron releasing para-substituents, thus imparting a double bond character to the aryl-I bond:⁴⁰



A similar d-orbital resonance may be visualized in the phenyl-p-anisyliodine as well as phenyl-p-tolyliodine. This would lead to a further strengthening of the tolyl carbon-I and anisyl carbon-I bonds, relative to the phenyl carbon-I bond:



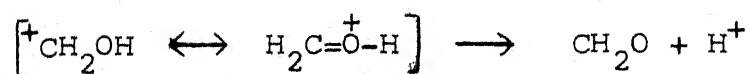
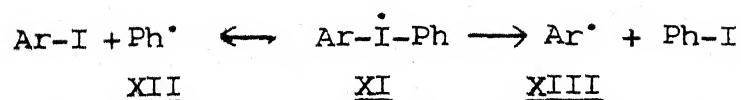
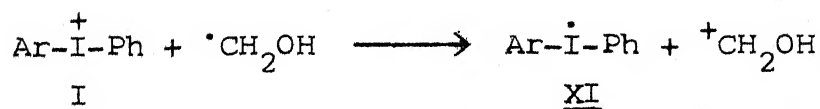
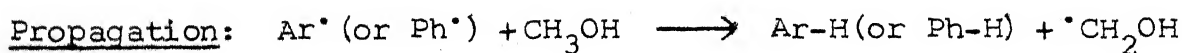
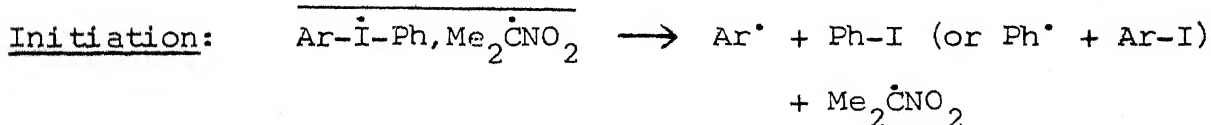
The 2-nitropropyl radical is stabilized by resonance. It would interact with the aryl radical, in the transition states V and VI, after considerable amount of bond lengthening of aryl C-I bond preparatory to homolysis has occurred and the aryl groups have acquired considerable amount of radical character.⁴¹ Thus, due to this large amount of bond lengthening at the transition state and the high electronegativity of 2-nitropropyl radical, dipolar structures IX and X would contribute towards stabilization^{41a} of resonance hybrids for the transition states V and VI, respectively.

IXX

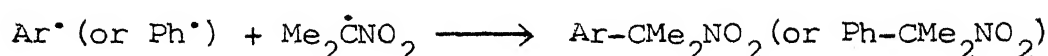
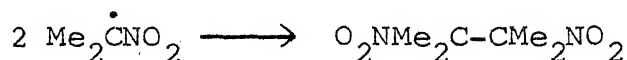
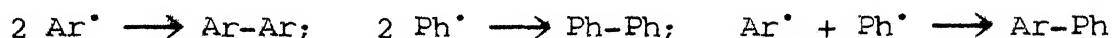
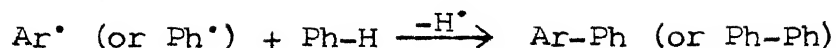
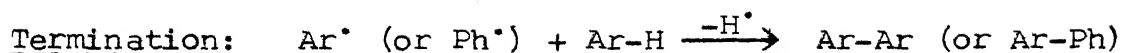
It is obvious that with electron donating substituents in the aryl ring, IX would be stabilized more than X, and thus the transition states in the reactions of phenyl-p-tolyliodonium cation and phenyl-p-anisylidonium cation would resemble V more than VI. This accounts for the high ratios of the products VII:VIII, actually observed in runs 6 and 9, respectively.

The radicals escaping from the cage IV, initiate a concurrent chain process outlined in Scheme II.9, accounting for the remaining products:

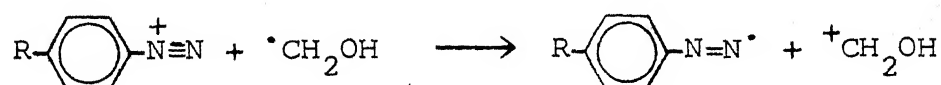
SCHEME II.9



...contd.

Scheme II.9 (contd.)

The chain is propagated by a hydrogen atom abstraction from methanol giving hydroxymethyl radical and subsequent electron transfer from this radical ($^\bullet\text{CH}_2\text{OH}$) to the diaryliodonium cation I. Such an electron transfer from the hydroxymethyl radical is preceded in the reactions of arenediazonium salts in methanol medium:^{42,43}

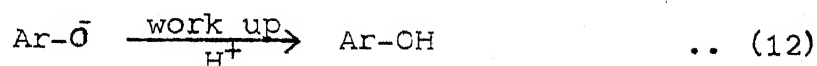
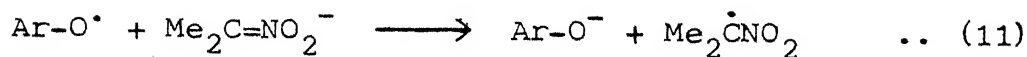
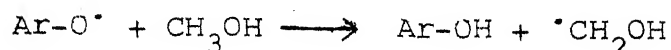
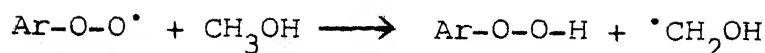
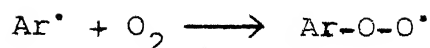


The ratios of the products: benzene/anisole in run 9 and benzene/toluene in run 6 are very close to unity. This lack of discrimination in the formation of aryl radicals has been observed²⁸ in other radical reactions of diaryliodonium salts, and may be due to the compensation of higher anisyl C-I and tolyl C-I bond dissociation energies relative to the phenyl C-I bond dissociation energy, by the higher stabilities of the $\text{p-CH}_3\text{O-C}_6\text{H}_4^\bullet$ and $\text{p-Me-C}_6\text{H}_4^\bullet$ radicals compared to the Ph^\bullet radical.⁴⁴ The enhanced stabilities of these aryl radicals

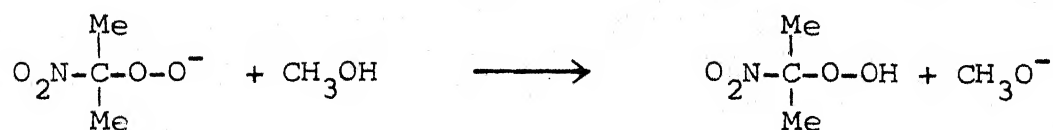
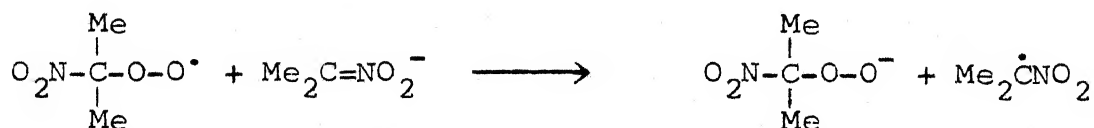
are apparently due to an increase in delocalization of the odd electron, brought about by bond bending in the σ aryl radicals, which leads to a competition for the odd electron between a localized p orbital and a delocalized p orbital.⁴⁵ The intervention of diaryliodine XI in the formation of aromatic monomeric hydrocarbons is further supported by the fact that the ratio of the products:benzene/anisole in run 9 is consistent with the relative concentrations of XII and XIII as produced from XI in the reported²² reduction of phenyl-p-anisylodonium cation with Ti(III).

Though α -methylstyrene effectively inhibits the chain mechanism, by scavenging the free aryl radicals, it is known not to significantly affect the cage processes.⁴⁶ Indeed, in its presence, more of the reaction with diphenyliodonium cation (run 4) proceeds by the radical cage process shown in Scheme II.8, leading to an increase in the yield of 2-phenyl-2-nitropropane, though the overall reaction is observed to be retarded.

Oxygen may inhibit the free radical chain mechanism by coupling with the aryl radicals to produce aryl hydroperoxides,⁴⁷ which decompose to give aryloxy radicals.⁴⁸ These aryloxy radicals may abstract hydrogen atoms from the molecules of methanol solvent to yield phenol as outlined in Scheme II.10. Alternatively, the aryloxy radical may accept an electron from the 2-nitropropanate anion giving an aryloxy anion which in the presence of a proton would give phenol (Eqns. 11 and 12):

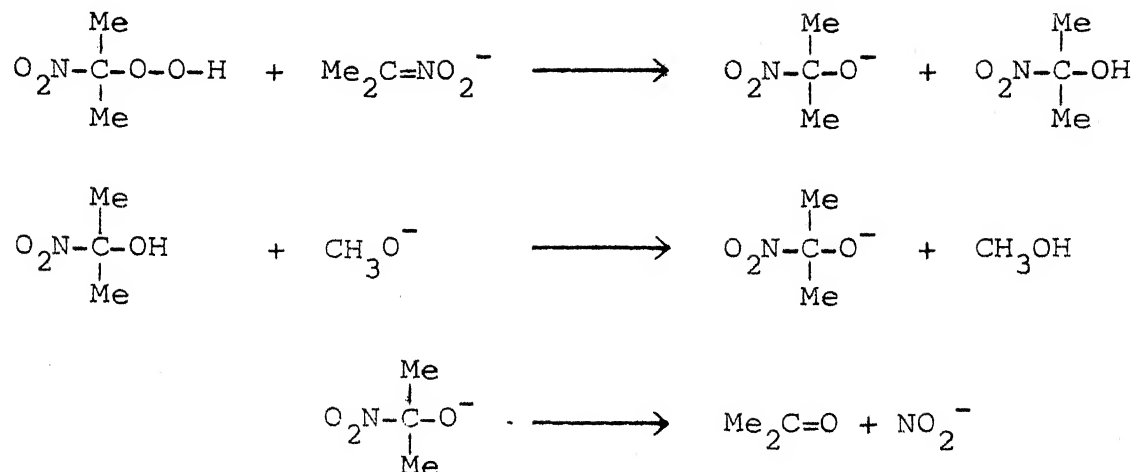
SCHEME II.10

Molecular oxygen may also couple with the 2-nitropropyl radical, yielding the corresponding peroxy radical, which reacts with the 2-nitropropanate anion by a chain process⁴⁹ resulting in the formation of acetone and NO_2^- anion, as outlined in Scheme II.11:

SCHEME II.11

(Scheme contd.)

(Scheme II.11) contd.



Such a process is known⁵⁰ to occur in other free radical reactions of 2-nitropropanate anion. Destruction of 2-nitropropanate anion reagent in this manner leads to inhibition of its reaction with diaryliodonium salts. Oxygen is also known to interfere with cage reactions.⁷

II.4 Experimental

All melting points were taken on MEL-TEMP melting point apparatus. IR spectra were recorded on Perkin-Elmer, model-521 infrared spectrophotometer. GLC analyses were carried out on a chromatography and company model AC1-FI chromatograph using 10% SE-30 on Crom-P (85-100M) column of 2m length. Column chromatography was done over activated basic alumina (E. Merck) column. Reaction products were identified by comparison of their retention times in GLC, IR spectra, thin layer chromatography in

comparison with those of the authentic samples, elemental analyses, melting or boiling points and mixed melting points. Literature melting or boiling points are cited from "Handbook of Chemistry and Physics," 50th edition, R.C. Weast (ed.), published by Chemical Rubber Co., Cleaveland, Ohio, unless otherwise stated.

Starting Materials

Diphenyliodonium bromide,⁵¹ phenyl-p-tolyliodonium bromide⁵¹ and phenyl-p-anisylidonium bromide⁵¹ were prepared by known procedures. Authentic samples of p-iodotoluene,⁵² p-iodoanisole,⁵² 4,4'-dimethylbiphenyl,⁵³ 4,4'-dimethoxybiphenyl,⁵³ 2,3-dinitro, 2,3-dimethylbutane⁵⁴ were also prepared by known methods. Authentic samples of benzene (BDH), toluene (BDH), anisole (Naarden Hall), iodobenzene (HPC) and 2-nitropropane (Pfoltz and Bauer Inc.) were used after distillation. Biphenyl (BDH) was used after recrystallization. α -Methylstyrene (BDH) and dimedone (BDH) were used without further purification.

Lithium 2-nitropropan-2-ide was prepared by the known procedure.⁵⁵

Preparation of absolute methanol⁵²

Dry magnesium turnings (5 g) and resublimed iodine (0.5 g) were placed in a 2 l RB flask fitted with a double surface reflux condenser. Methanol (60 ml) was added through the top

of the condenser and the mixture warmed over water-bath until the iodine disappeared. There was a vigorous evolution of hydrogen gas as soon as heating was started. Heating was stopped for some time but started again when evolution of hydrogen slowed down, to ensure that all the magnesium got converted into methoxide. An additional quantity of methanol (900 ml) was then added and the mixture refluxed for 30 min. Absolute methanol was collected by distillation using a Vigreux Column after discarding the first 25 ml of the distillate.

Preparation of deaerated methanol

Absolute methanol prepared by the above method was taken in a two necked RB flask, fitted with gas passing adapter and a gas outlet equipped with a mercury trap. The two necked flask was kept in an ice-bath mounted over a magnetic stirring base. Stirring was started and dry nitrogen gas passed through the solution for one hour. Finally, the flask was stoppered and sealed with parafilm. This deaerated methanol was used as the solvent in the reactions described below:

- (1) Reactions of diphenyliodonium bromide with lithium 2-nitropropan-2-ide
- (a) with diphenyliodonium bromide (0.005 mol) and lithium 2-nitropropan-2-ide in 1:2 molar ratio under nitrogen atmosphere at 30°C, under laboratory lights

In a 250 ml 3-neck RB flask, mounted over a magnetic stirring base, fitted with a device to pass pure dry nitrogen,

connected to a condenser and a mercury trap was placed a slurry of diphenyliodonium bromide (1.805 g; 0.005 mol) in 50 ml absolute deaerated methanol at room temperature (30°C). A solution of lithium 2-nitropropan-2-ide (0.95 g, 0.01 mol) in 50 ml absolute deaerated methanol was added through a pressure equalizing dropping funnel with continuous stirring. Nitrogen gas was passed throughout the reaction period. The reaction mixture slowly turned yellow in color. Fixed aliquots of the reaction mixture were removed by a syringe from time to time and treated with saturated potassium iodide solution to precipitate the unreacted diphenyliodonium cation as its iodide. The reaction was found to be complete after 48 hr when a sample of the reaction mixture gave no precipitate with KI solution.

The reaction mixture was then poured into 250 ml of water and a 50 ml portion of this solution was immediately used for the determination of formaldehyde. The remaining quantity of the solution was extracted with ether (4 x 50 ml). The combined ethereal extract was dried (anhydrous MgSO_4), filtered and carefully concentrated under reduced pressure at room temperature to a volume of 50 ml. This crude mixture was analyzed by GLC using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length. The products were identified by comparison of their retention times with those of the authentic samples and the yields were determined by comparing the peak areas with those of the authentic samples. The yields of various products, after taking into consideration the amount of reaction mixture used for the

determination of formaldehyde, were: benzene (43%), iodobenzene (94%), biphenyl (5%) and 2,3-dinitro, 2,3-dimethylbutane (5%). Complete removal of the solvent thereafter, gave a crude mixture which was dissolved in an equal volume of petroleum ether (b.p. 60-80°C) and was passed through a column of activated basic alumina. Elution with petroleum ether (b.p. 60 - 80°C) first gave a mixture of benzene, iodobenzene and biphenyl. Further elution with benzene-petroleum ether (b.p. 60 - 80°C) (1:4) yielded 2-phenyl-2-nitropropane. Reduced pressure evaporation of the benzene/petroleum ether solution at room temperature yielded 2-phenyl-2-nitropropane (0.339 g, ca. 41%) identified by comparison of its IR spectra with that of an authentic sample and by its elemental analysis.

Estimation of formaldehyde: To the 50 ml of the solution taken for the estimation of formaldehyde, an aqueous saturated solution of dimedone (50 ml) was added. After stirring for 6 hours, the mixture was allowed to stand for 40 hr. The precipitated dimedone derivative of formaldehyde was separated by filtration and dried at 60°C. It was characterized by mixed melting point and its superimposable IR spectrum with that of an authentic sample. Yield of this derivative corresponded to a total of 38% of formaldehyde formed.

(b) with equimolar ratio of reactants (0.005 mol each) in nitrogen atmosphere at 30°C under laboratory lights

A slurry of diphenyliodonium bromide (1.805 g; 0.005 mol) in 50 ml of methanol was reacted with a solution of lithium

2-nitropropan-2-ide (0.475 g, 0.005 mol) in methanol (50 ml) at 30°C, keeping all other conditions the same as described for reaction 1(a). After 48 hr, the reaction mixture was poured into a saturated aqueous solution of potassium iodide (200 ml) in order to precipitate out the unreacted diphenyliodonium cation as its iodide. The precipitate was filtered, washed in turn with water, methanol and ether and dried under vacuum. This yielded 0.612 g (30%) of diphenyliodonium iodide, m.p. 173°C(dec); lit.⁵¹ m.p. 173°-175°C(dec). The total volume of the mother liquor left after removal of the precipitate was made upto 250 ml by adding water. A 50 ml portion of this solution was immediately used for the determination of formaldehyde. The remaining solution was extracted with ether. The ethereal extract was dried and concentrated in the usual manner. The concentrate was analyzed by GLC using 10% SE-30 on Crom-P (85-100 M) column of 2 m length, and column chromatography in the same way as described under experiment 1(a). The product distribution was benzene (ca. 38%), iodobenzene (ca. 70%), biphenyl (ca. 3%), 2,3-dinitro-2,3-dimethylbutane (ca. 2%) and 2-phenyl-2-nitropropane (0.182 g; ca. 22%). The yield of formaldehyde estimated as its dimedone derivative was ca. 32%.

- (c) with diphenyliodonium bromide (0.005 mol) and lithium 2-nitropropan-2-ide in 1:2 molar ratio in oxygen atmosphere at 30°C, under laboratory lights

A slurry of diphenyliodonium bromide (1.805 g; 0.005 mol) in 50 ml methanol was reacted with a solution of lithium 2-nitropropan-2-ide (0.95 g; 0.01 mol) in methanol (50 ml) at 30°C.

Dry oxygen gas was bubbled through the reaction mixture. All other conditions were kept the same as for the reaction 1(a). After 96 hr, the reaction mixture was poured into a saturated aqueous solution of potassium iodide (200 ml), in order to precipitate the unreacted diphenyliodonium cation as its iodide. The precipitate was filtered, washed in turn with water, methanol and ether and dried under vacuum. This yielded 1.632 g (80%) of diphenyliodonium iodide m.p. $174^{\circ}\text{C}(\text{dec})$, lit. m.p. $173-175^{\circ}\text{C}(\text{dec})$ ⁵¹. The total volume of the mother liquor left after removal of the precipitate was made upto 250 ml by adding water. A 50 ml portion of this solution was immediately used for the determination of formaldehyde. The remaining solution was extracted with ether and the extract washed, dried and concentrated as usual. The concentrate was analyzed by GLC using 10% SE-30 on Crom-P (85-100 M) column of 2 m length and column chromatography in the same way as described for the reaction 1(a). The product distribution was: benzene (ca. 5%), phenol (ca. 9%), iodobenzene (ca. 18%) and 2-phenyl-2-nitropropane (0.05 g; ca. 6%). No precipitate (of the dimedone derivative of formaldehyde) formed even after the solution was kept aside for 80 hr.

- (d) with diphenyliodonium bromide (0.005 mol) and lithium 2-nitropropan-2-ide in 1:2 molar ratio in nitrogen atmosphere at 30°C under laboratory lights with added α -methylstyrene (0.01 mol)

Diphenyliodonium bromide (1.805 g; 5×10^{-3} mol) and α -methylstyrene (1.182 g; 0.01 mol) taken together in 50 ml methanol were allowed to react with lithium 2-nitropropan-2-ide

(0.95 g; 0.01 mol) in 50 ml methanol at 30°C under nitrogen atmosphere in a similar way as described under the experiment 1(a). After 48 hr, the reaction mixture was poured into a saturated aqueous solution of KI (200 ml). The precipitate obtained was filtered, washed in turn with water, methanol and ether and dried under vacuum. This yielded 0.204 g (10%) of diphenyliodonium iodide, m.p. 173°C (dec); lit. m.p. 173°-175°C (dec). The total volume of the mother liquor, left after removal of the precipitate was made upto 250 ml by adding water. A 50 ml portion of this solution was immediately used for the determination of formaldehyde. The remaining solution was extracted with ether and the ethereal extract dried and concentrated in the usual manner. The concentrate was analyzed by GLC using 10% SE-30 on Crom-P (85-100 M) column of 2 m length and column chromatography in the same way as described for the reaction 1(a). The product distribution obtained was benzene (8%), iodobenzene (88%), an unestimated amount of α -methylstyrene, biphenyl (2%), 2,3-dinitro-2,3-dimethylbutane (2%) and 2-phenyl-2-nitropropane (0.553 g; ca. 67%). No precipitate of the dimedone derivative of formaldehyde was obtained.

(e) with diphenyliodonium bromide (5×10^{-3} mol) and lithium 2-nitropropan-2-ide in 1:2 molar ratio under nitrogen atmosphere at 30°C in complete darkness

Diphenyliodonium bromide (1.805 g; 5×10^{-3} mol) contained in 50 ml methanol and lithium 2-nitropropan-2-ide (0.95 g; 0.01 mol) dissolved in 50 ml methanol were reacted in dark (the reaction

48 hr. The reaction mixture was then poured into 250 ml of water. A 50 ml portion of this solution was immediately used for the estimation of formaldehyde and the rest of the solution was extracted with ether (4 x 50 ml). The ethereal extract was dried (anhydrous MgSO_4), filtered and concentrated as described for the reaction 1(a). The concentrated crude mixture of products was analyzed by GLC using 10% SE-30 on Crom-P (85-100 M) column of 2 m length. The products were identified by comparison of their retention times with those of the authentic samples and the yields were determined by comparing the peak areas with those of the authentic samples. The yields of various products identified were: benzene (23%), toluene (21%), iodobenzene (44%), p-iodotoluene (54%), biphenyl (3%), di-p-tolyl (2%), a trace of p-methylbiphenyl and 2,3-dinitro-2,3-dimethylbutane (6%). This mixture was then concentrated further and charged on a column of activated basic alumina. Elution with petroleum ether (b.p. 60-66°C) first gave a mixture of benzene, toluene, iodobenzene and a mixture of biaryls. Further elution of the column with the same solvent gave p-iodotoluene b.p. 210°C; lit. b.p. 211°-212°C (0.588 g, ca. 54%). Later, elution with a mixture of petroleum ether (b.p. 60-80°C) and benzene (10:1) gave 2-phenyl-2-nitropropane (0.198 g, ca. 24 %) and 2-(p-tolyl)-2-nitropropane (0.143 g, ca. 16%), identified by comparison of their IR spectra with those of the authentic samples and by elemental analyses. The yield of formaldehyde estimated as its dimedone derivative was 37% (based on phenyl-p-tolylodonium bromide).

(b) with phenyl-p-tolyliodonium bromide (5×10^{-3} mol) and lithium 2-nitropropan-2-ide in 1:2 molar ratio in oxygen atmosphere at 30°C, under laboratory lights

Phenyl-p-tolyliodonium bromide (1.875 g; 5×10^{-3} mol) contained in 50 ml methanol was allowed to react with lithium 2-nitropropan-2-ide (0.95 g; 0.01 mol) in 50 ml methanol at 30°C. Dry oxygen gas was bubbled through the reaction mixture; but all other conditions were kept the same as for the reaction 2(a). After 96 hr, the reaction mixture was poured into a saturated aqueous solution of KI (200 ml) to precipitate the unreacted phenyl-p-tolyliodonium cation as its iodide. The precipitate obtained was filtered, washed in turn with water, methanol and ether and dried under vacuum. This yielded phenyl-p-tolyliodonium iodide (1.688 g; 80%); m.p. 153°C; lit.⁵⁶ m.p. 153°-154°C. The total volume of the mother liquor, left after removal of the precipitate, was made upto 250 ml, by adding water. A 50 ml solution was used immediately for the estimation of formaldehyde. The remaining solution was extracted with ether (4 x 50 ml) and the ethereal extract washed, dried (anhydrous MgSO_4) and concentrated in the usual manner. The product mixture on GLC analyses and subsequent column chromatography as described for the reaction 2(a), yielded benzene (4%), toluene (4%), phenol (4%), iodobenzene (8%), p-cresol (4%), p-iodotoluene (10%), 2-phenyl-2-nitropropane (0.025 g; 3%) & 2-(p-tolyl)-2-nitropropane (0.018 g; ca. 2%). No precipitate of the dimedone derivative of formaldehyde was obtained.

(c) with phenyl-p-tolyliodonium bromide (5×10^{-3} mol) and lithium 2-nitropropan-2-ide in 1:2 molar ratio under nitrogen atmosphere at 30°C in complete darkness

A slurry of phenyl-p-tolyliodonium bromide (1.875 g; 5×10^{-3} mol) in methanol (50 ml) was reacted with a solution of lithium 2-nitropropan-2-ide (0.95 g; 0.01 mol) in 50 ml methanol at 30°C, under nitrogen atmosphere in complete darkness (the reaction flask was wrapped in black paper). The reaction mixture was poured into a saturated aqueous solution of KI (200 ml), after 48 hr to precipitate the unreacted phenyl-p-tolyliodonium cation as its iodide. This yielded phenyl-p-tolyl-iodonium iodide (0.253 g, 12%); m.p. 152°C; lit.⁵⁶ m.p. 153°-154°C. The mother liquor was diluted and extracted as described for the reaction 1(b). The ethereal extract, so obtained, was washed, dried (anhydrous MgSO_4), filtered and concentrated. The concentrate was analyzed by GLC and column chromatography as described for the reaction 2(a). The product distribution obtained was benzene (20%), toluene (18%), iodobenzene (38%), p-iodotoluene (47%), biphenyl (2%), di-p-tolyl (2%), a trace of p-methylbiphenyl, 2,3-dinitro-2,3-dimethylbutane (5%), 2-phenyl-2-nitropropane (0.173 g; ca. 21%) and 2-(p-tolyl)-2-nitropropane (0.125 g; ca. 14%). The yield of formaldehyde, estimated as its dimedone derivative was 32%.

3. Reactions of phenyl-p-anisylodonium bromide with lithium 2-nitropropan-2-ide

- (a) with phenyl-p-anisylodonium bromide (5×10^{-3} mol) and lithium 2-nitropropan-2-ide in 1:2 molar ratio in nitrogen atmosphere at 30°C, under laboratory lights

A slurry of phenyl-p-anisylodonium bromide (1.955 g; 5×10^{-3} mol) in 50 ml methanol was reacted with a solution of lithium 2-nitropropan-2-ide (0.95 g; 0.01 mol) in 50 ml methanol at 30°C, under nitrogen atmosphere, in a manner similar to that described for the reaction 1(a). The reaction was found to be complete in 48 hr, as a small sample of the reaction mixture did not give any precipitate with saturated aqueous solution of KI. The reaction mixture was poured into 250 ml water. A 50 ml portion of this solution was immediately used for the estimation of formaldehyde. The rest of the solution was extracted with ether (4 x 50 ml). The combined ethereal extract was washed, dried over anhydrous MgSO_4 , filtered and concentrated to 50 ml, as described for the reaction 1(a). This concentrate was analyzed by GLC using 10% SE-30 on Crom-P (85-100 M) column of 2 m length. The products were identified by a comparison of their retention times with those of the authentic samples and the yields were determined by comparing the peak areas with those of the standard authentic samples. The yields of various products identified were: benzene (23%), anisole (18%), iodobenzene (38%), p-methoxyiodobenzene (57%), biphenyl (3%), di-p-anisyl (3%), a trace of p-methoxybiphenyl and 2,3-dinitro-2,3-dimethylbutane (5%). The ethereal extract was then concentrated further and

charged over a column of activated basic alumina. Elution with petroleum ether (b.p. 60-66°C) first gave a mixture of benzene, anisole, iodobenzene and biaryls. Further elution of the column with petroleum ether (60-80°C) gave p-iodoanisole (0.667 g, 57%) m.p. 51°C; lit. m.p. 51-52°C. Later, elution with a mixture of petroleum ether (b.p. 60-80°C) and benzene (4:1) gave 2-phenyl-2-nitropropane (0.231 g; ca. 28%) and 2-(p-anisyl)-2-nitropropane (0.127 g; ca. 13%), identified by comparison of their IR spectra with those of the authentic samples and by their elemental analyses. The yield of formaldehyde estimated as its dimedone derivative was found to be 35% (based on phenyl-p-anisylodonium bromide).

(b) with phenyl-p-anisylodonium bromide (5×10^{-3} mol) and lithium 2-nitropropan-2-ide in 1:2 molar ratio in oxygen atmosphere at 30°C, under laboratory lights.

A slurry of phenyl-p-anisylodonium bromide (1.955 g; 5×10^{-3} mol) in 50 ml methanol was reacted with lithium 2-nitropropan-2-ide (0.95 g; 0.01 mol) dissolved in 50 ml of methanol at 30°C. Oxygen was continuously bubbled through the reaction mixture, which was stirred for 96 hr under the conditions described for the previous reaction. At the end of this period, the reaction mixture was poured into a saturated aqueous solution of potassium iodide (200 ml) to precipitate the unreacted phenyl-p-anisylodonium cation as its iodide. The precipitate, so obtained, was filtered, washed in turn with water, methanol and ether and dried under vacuum. This yielded phenyl-p-anisylodonium iodide (1.662 g, 85%); m.p. 163°C; lit.⁵¹ m.p. 162.5 to

163.5°C. The mother liquor left after the removal of this precipitate, was diluted and extracted as described under the reaction 1(c). The ethereal extract was washed, dried (anhydrous MgSO_4) and concentrated in the usual manner. The product mixture on GLC analyses and subsequent column chromatography as described for the reaction 3(a) yielded benzene (4%), anisole (4%), phenol (5%), iodobenzene (6%), p-methoxyiodobenzene (8%), p-methoxyphenol (4%), 2-phenyl-2-nitropropane (0.017 g; ca. 2%) and 2-(p-anisyl)-2-nitropropane (0.02 g; ca. 2%). No precipitate of the dimedone derivative of formaldehyde was obtained.

(c) with phenyl-p-anisyliodonium bromide (5×10^{-3} mol) and lithium 2-nitropropan-2-ide in 1:2 molar ratio under nitrogen atmosphere at 30°C in complete darkness

A slurry of phenyl-p-anisyliodonium bromide (1.955 g; 5×10^{-3} mol) in 50 ml methanol was reacted with lithium 2-nitropropan-2-ide (0.95 g; 0.01 mol) dissolved in 50 ml methanol, in complete darkness under otherwise identical conditions as those described for the reaction 3(a) (the reaction flask was wrapped in black paper). The reaction remained incomplete in 48 hr. At the end of 48 hr, the reaction mixture was poured into a saturated aqueous solution of KI (200 ml) to precipitate the unreacted phenyl-p-anisyliodonium cation as its iodide. This yielded, after filtration, washing and drying in vacuum, phenyl-p-anisyliodonium iodide (0.329 g; ca. 15%); m.p. 162°C; lit.⁵¹ m.p. 162.5 - 163.5°C. The mother liquor was diluted and extracted as described previously for the reaction 1(b). The ethereal extract,

so obtained, was washed, dried (anhydrous MgSO_4), filtered and concentrated. This concentrate was analyzed by GLC and column chromatography as described for the reaction 3(a). The product distribution obtained was: benzene (18%), anisole (15%), iodobenzene (33%), p-methoxyiodobenzene (50%), biphenyl (ca. 2%), di-p-anisyl (ca. 2%), a trace of p-methoxybiphenyl, 2,3-dinito-2,3-dimethylbutane (5%), 2-phenyl-2-nitropropane (0.206 g; ca. 25%) and 2-(p-anisyl)-2-nitropropane (0.107 g; ca. 11%). The yield of formaldehyde estimated as its dimedone dierivative was 30%.

II.5 References

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CHAPTER III

RADICAL NUCLEOPHILIC SUBSTITUTION MECHANISMS IN THE REACTIONS OF ARENE- DIAZONIUM CATIONS WITH NITRITE AND 2-NITROPROPANATE ANIONS

III.1 Abstract

The undesirable effects of an excess of nitrite ion on the yields of arenediazonium salts, in the diazotization of primary aromatic amines, arises due to the formation of reactive aryl radicals in a subsequent reaction between the arenediazonium salt and the nitrite ion. A study of the reactions of benzenediazonium fluoroborate, p-nitrobenzenediazonium fluoroborate and p-methoxybenzenediazonium fluoroborate with sodium nitrite has been conducted in methanol solvent at 0°C, under varying conditions. Although the arenediazonium fluoroborates under study are stable in methanol for at least 2 hr at 0°C, the addition of sodium

nitrite results in an instantaneous evolution of nitrogen gas yielding protodediazoniated products and nitroarenes besides biaryls, phenols and formaldehyde. The reaction with p-nitrobenzenediazonium fluoroborate is faster and that with p-methoxybenzenediazonium fluoroborate slower compared to the reaction with benzenediazonium fluoroborate. These reactions are catalyzed by light as well as Cu(II) ions and retarded by the presence of molecular oxygen. The intermediacy of aryl cations or aryne intermediates in these reactions has been ruled out; but the intervention of radicals has been established. The possibility of formation of free radicals via covalent diazonitrite intermediates has been eliminated. A free radical chain mechanism initiated by the transfer of an electron from the nitrite ion to the LUMO of arenediazonium cation and proceeding via the formation of nitroarene radical anion intermediates has been proposed to account for the observed facts.

The reactions of the same three arenediazonium fluoroborates with the 2-nitropropanate anion have also been examined. Though benzenediazonium fluoroborate and p-methoxybenzenediazonium fluoroborate react with lithium 2-nitropropan-2-ide in methanol at 0°C under nitrogen atmosphere, to yield benzeneazo-2-(2-nitro)propane and p-methoxybenzeneazo-2-(2-nitro)propane, respectively, p-nitrobenzenediazonium fluoroborate under similar conditions yields both the azo-coupling as well as the dediazonation products. Occurrence of dediazonation via an S_NAr pathway or by the decomposition of the azo-coupling product,

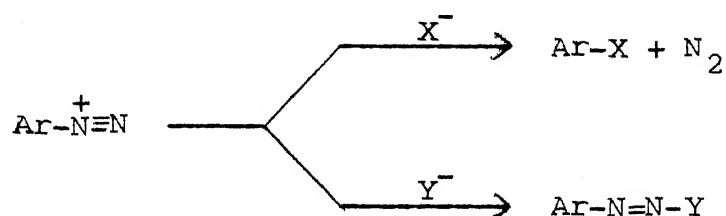
p-nitrobenzeneazo-2-(2-nitro) propane has been considered unlikely. While the covalent azo compounds are produced by the ionic coupling, a parallel free radical chain mechanism has been proposed to account for the formation of other products. The effect of Cu(I) on these reactions has also been examined. In the presence of Cu(I), even benzenediazonium fluoroborate and p-methoxybenzenediazonium fluoroborate partly react with 2-nitropropanate anion by the electron transfer mechanism involving evolution of nitrogen gas. This constitutes a new example of an entrainment process.

III.2 Introduction

Arenediazonium salts are versatile synthetic reagents,¹⁻⁴ useful both in the laboratory and industry. Reactions of these compounds have also contributed immensely to the knowledge of chemical theory.⁵ The first aromatic diazo compound was prepared and studied by Griess⁶ in 1858. The structure of these compounds is known to depend on pH of the medium.⁷ In acidic medium, many arenediazonium compounds have ionic structures like $\text{Ar}-\overset{+}{\text{N}}\equiv\text{NX}^-$. Unionized derivatives such as the diazocyanides, $\text{Ar}-\text{N}=\text{N}-\text{C}\equiv\text{N}$ are also known.⁸ Though unexpected, diazonium compounds are also known to occur in nature.⁹ The properties and reactions of arenediazonium compounds have been extensively reviewed.^{10,11}

A majority of chemical reactions of arenediazonium compounds can be put under two general categories. In the reactions of first category, the diazo group is replaced by another atom or a group of atoms, with the evolution of nitrogen gas. The reactions of second category result in the formation of a new bond at the beta-nitrogen. The reactions under the two categories are depicted in Scheme III.1:

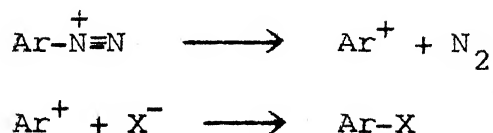
SCHEME III.1



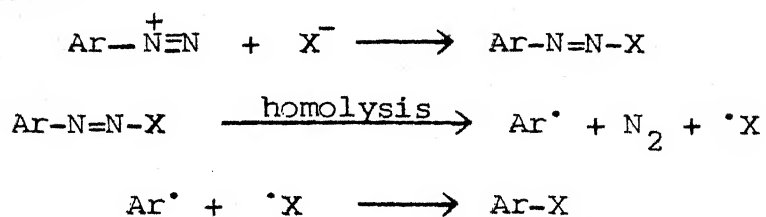
In most of their reactions involving ejection of nitrogen, arenediazonium salts have been viewed in the literature¹⁰⁻¹³ to act as precursors of either aryl cations or aryl radicals, via the pathways shown in Scheme III.2:

SCHEME III.2

S_N1 mechanism:



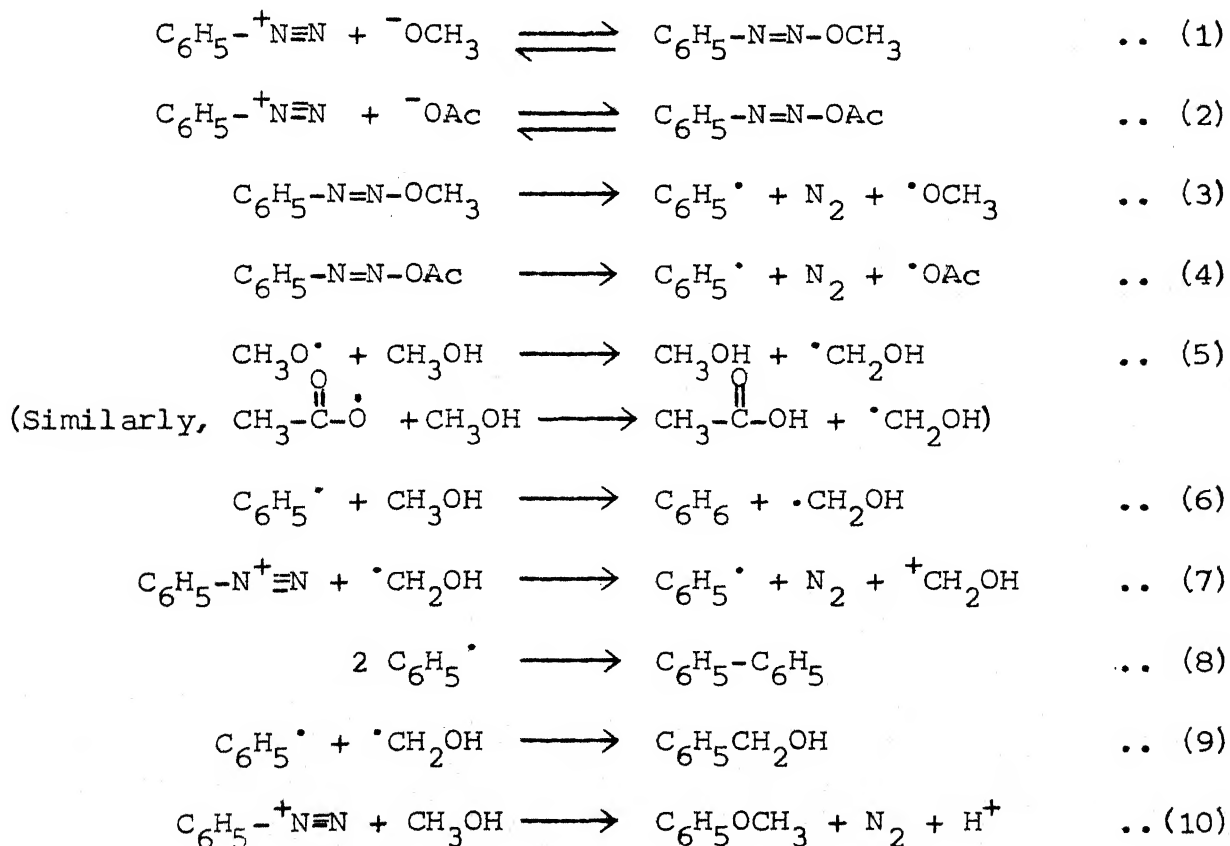
Homolytic mechanism:



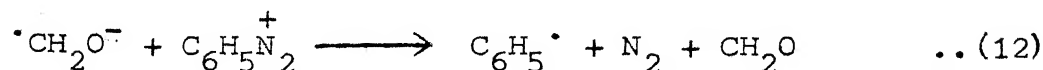
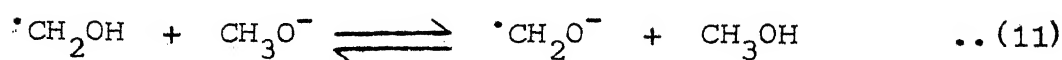
Although the reactions of arenediazonium cations involving aryl cation intermediates have been examined in great detail in the past, those involving aryl radicals have attracted the attention of chemists relatively recently.

The fate of arenediazonium cations in basic media has been examined in detail. Under these conditions, the arenediazonium cations are known to react by a free radical mechanism.¹⁴⁻¹⁶ Thus, for the reactions of arenediazonium salts with alcohols at high pH and in the presence of acetate buffers, a free radical chain mechanism outlined in Scheme III.3, has been proposed:¹⁷⁻¹⁹

SCHEME III.3



Bunnett and coworkers²⁰⁻²² have also examined the above reactions and their conclusions also support this mechanism, with the exception that these authors prefer Eqns. (11) and (12) over Eqn. (7):

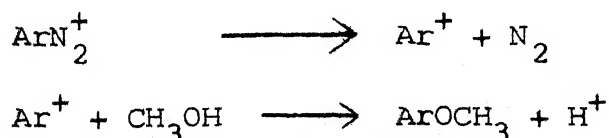


The kinetics of the reactions of arenediazonium cations with methoxide ion yielding syn- and anti-diazomethoxides have also been studied.^{23, 24}

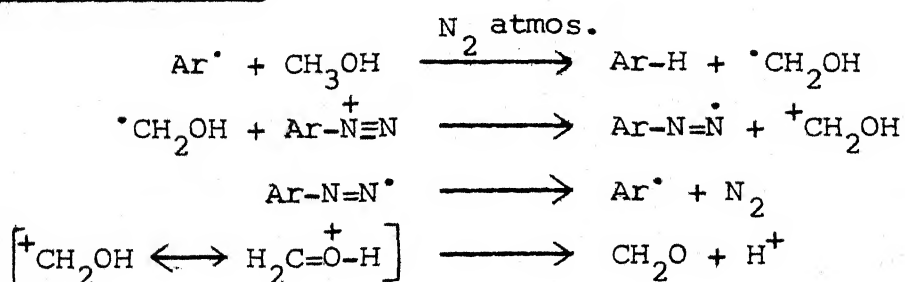
In acidic methanol, arenediazonium cations are known to undergo thermolysis at 80°C by a S_N1 mechanism under oxygen atmosphere and by a free radical process under nitrogen atmosphere.²⁵ Independent competitive pathways have been proposed^{26, 27} for the formation of protodediazoniated products and arylalkyl ethers (Scheme III.4):

SCHEME III.4

S_N1 mechanism:



Free radical mechanism:



Mode of initiation of the free radical chain is not clear, but electron transfer from methanol to the arenediazonium cation has been proposed by Bunnett and Yijima.²⁶ In aqueous ethanol also, arenediazonium salts, are reported²⁸ to decompose via free radical intermediates.

Protodediazoniation of arenediazonium cations has been accomplished by the use of reducing agents like hypophosphorous acid,^{29,30} zinc in alcohol,³¹⁻³² ethers,³³ ferrous sulphate,³⁴ rhodium complexes³⁵ and sodium borohydride. Most of these reactions involve aryl radicals as intermediates; but in the reductions by NaBH_4 ,³⁶⁻³⁸ radicals as well as aryl anions have been proposed.

Arenediazonium fluoroborates and salts of other fluoroacids are known³⁹⁻⁴² to yield aryl fluorides on thermal decomposition. Both free radical^{39,43} and ionic^{39,44} mechanisms have been proposed. The reactions of chloride and bromide ions with arenediazonium salts have been suggested to follow concerted bimolecular⁴⁵ as well as free radical⁴⁶ mechanisms; but nucleophilic displacement of nitrogen has been ruled out.⁴⁷ These reactions are generally carried out in the presence of copper or cuprous halides (Sandmeyer reaction).⁴⁸⁻⁵¹

Polarographic reduction^{52,53} of arenediazonium cations, generating diazenyl radicals (Scheme III.5), gives the first wave at a cathode potential around -0.55 volt. These reductions also show a second wave at relatively higher cathode potentials.

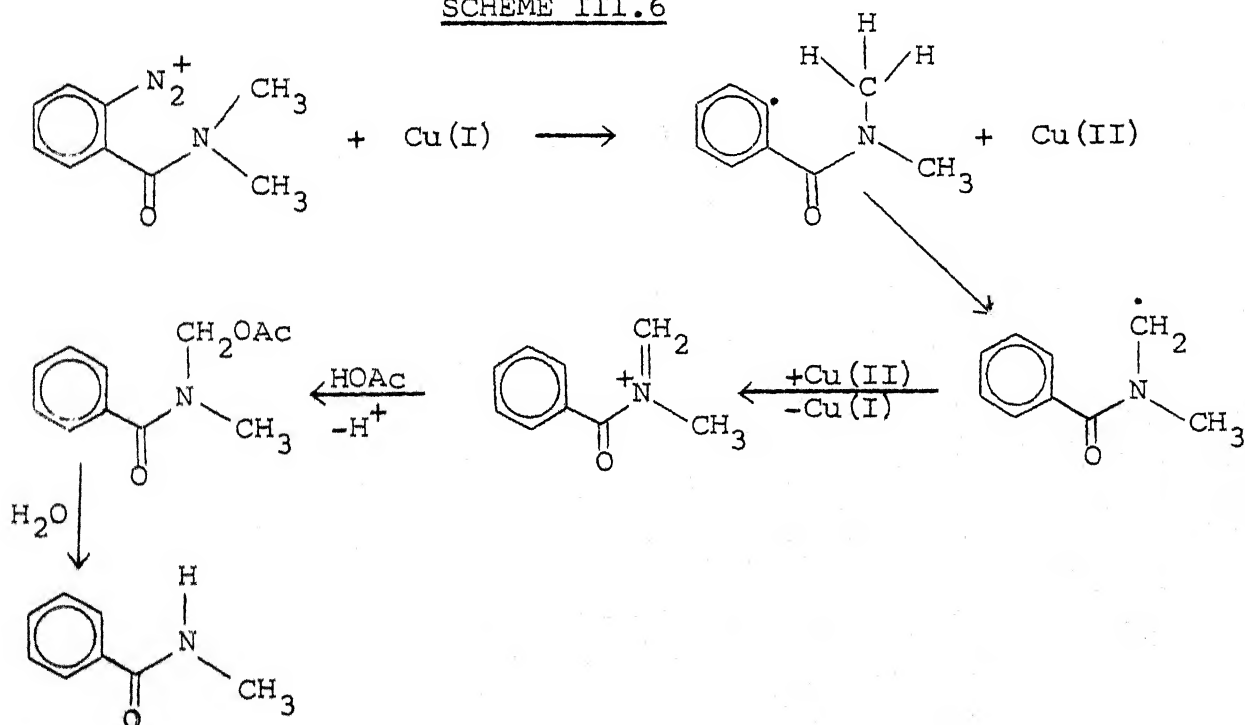
SCHEME III.5



The coulometric studies⁵⁴ on these cations also support the results obtained from polarographic reductions.

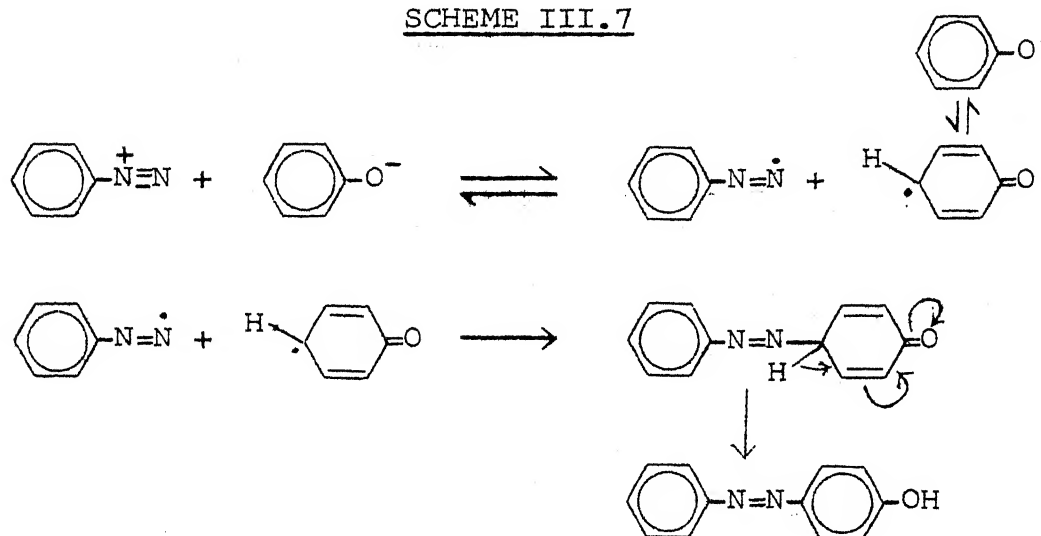
In view of the high electron affinity of arenediazonium cations, recent interest on the reactions of these, has been mainly centred around the possibility of generating aryl radicals via electron transfer processes. Thus copper(I) salts have been effectively used^{51,55-57} for the one electron reduction of arenediazonium cations. For example, Cu(I) catalyzed decomposition of the diazonium salt of ortho-amino-N,N-dimethylbenzamide⁵⁸ leads to the formation of a free radical, which undergoes facile 1,5-hydrogen shift giving, after work up, N-methylbenzamide, according to Scheme III.6:

SCHEME III.6



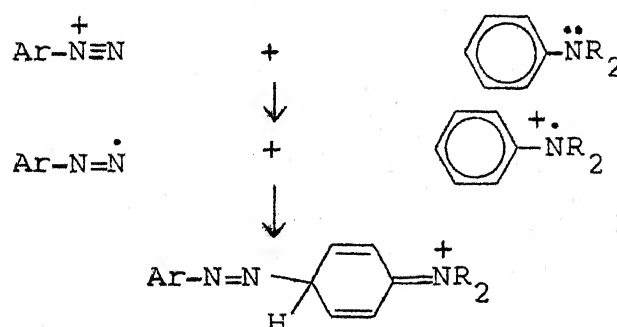
Single electron reductions of arenediazonium cations by sodium dithionite,⁵⁹ titanium(III),⁶⁰ copper,^{55,58,61} or radicals^{60a} such as $\cdot\text{CH}_2\text{OH}$, $\cdot\text{CHMeOH}$, $\cdot\text{CMe}_2\text{OH}$ and $\cdot\text{CO}_2\text{H}$ are known to generate aryl radicals.⁶² The reaction of phenoxide anion with the benzenediazonium cation producing 4-hydroxyazobenzene has been found⁶³ to proceed via an electron transfer free radical mechanism outlined in Scheme III.7:

SCHEME III.7



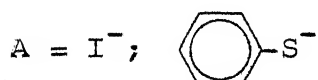
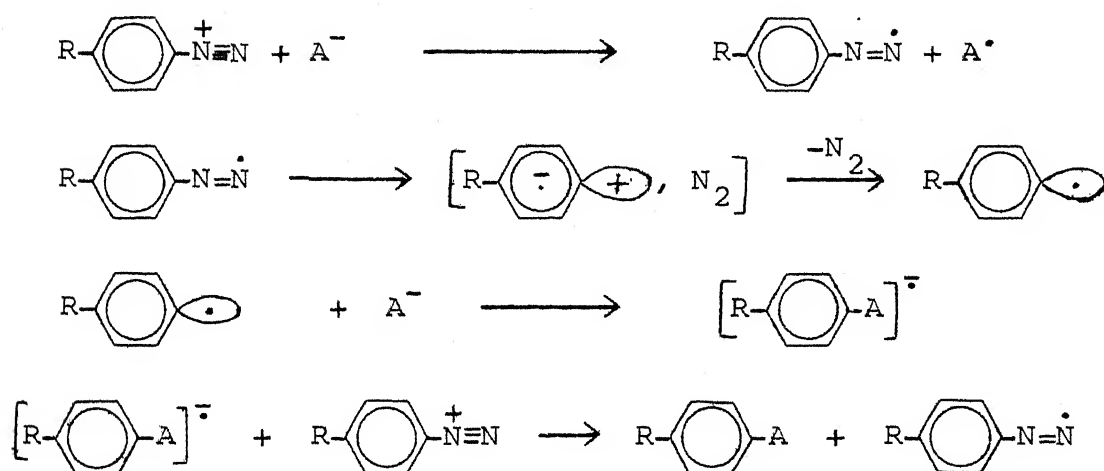
The first step in the reactions of aromatic amines with arenediazonium cations has been shown⁶⁴ by ESR studies to be an electron transfer from the former to the latter (Scheme III.8):

SCHEME III.8



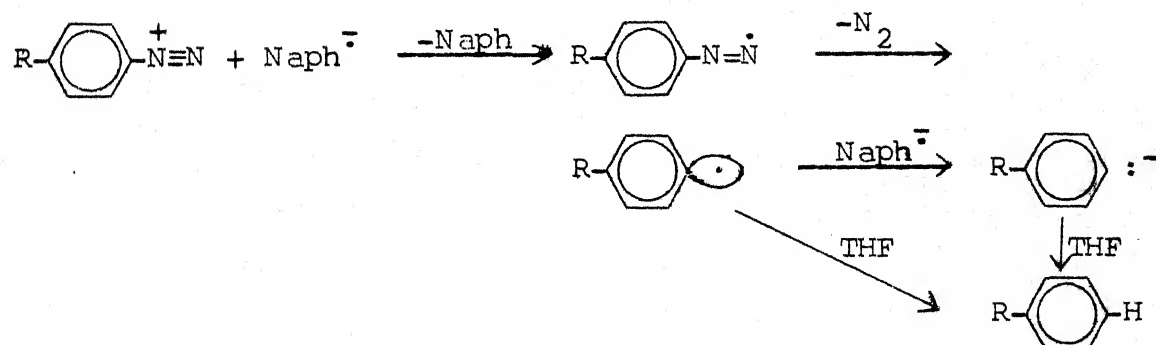
The reactions of arenediazonium fluoroborates with iodide,⁶⁷ thiophenoxide⁶⁷ and 2,4,6-tri-tert.butylphenoxide anions have been demonstrated by Singh and coworkers to proceed through free radical chain processes wherein the significant first step is the transfer of an electron from the anion to the arenediazonium cation. The mechanism proposed is outlined in Scheme III.9:

SCHEME III.9



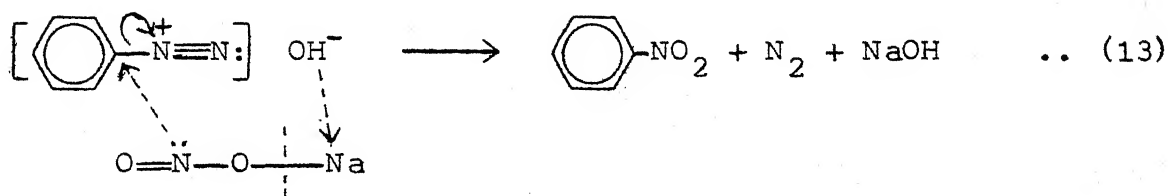
The reactions of arenediazonium cations with sodium naphthalene have also been shown⁶⁸ in our laboratory to occur by initial transfer of an electron to the diazonium cation. Different steps of these reactions are outlined in Scheme III.10:

SCHEME III.10



The replacement of the diazo group by a nitro group has been attempted by Sandmeyer,⁶⁹ Meisenheimer and coworkers,⁷⁰ Vesely and Dvorak,⁷¹ Orton,⁷² Bucherer and Van der Recke,⁷³ Hantzsch and Blagden,⁷⁴ and Contardi.⁷⁵ In each case, however, the reactions were of limited application.¹⁰ Many variations including the use of catalysts, have been suggested with a view to improving the yields.⁷⁶⁻⁸⁵ Methods of preparation of nitro compounds by the replacement of a diazo group have been reviewed.⁸⁶

The reaction between sodium nitrite and a diazo compound in dilute sodium hydroxide was suggested by Hodgson⁸⁷ to involve an attack of the anionoid O-N=O group at the carbon atom bonded to nitrogen (Eqn. 13):

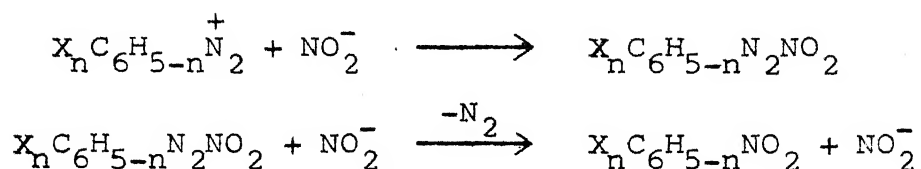


The adverse effect of an excess of sodium nitrite during the diazotization of an aryl amine⁸¹ mentioned previously in Section III.1 is thought to arise as a result of the reaction of former with arenediazonium salts producing reactive aryl radicals, which attack various compounds present in the medium to give complicated mixture of products.⁸⁸ The formation of biphenyl in the reaction of benzenediazonium fluoroborate with the nitrite anion⁸⁷ leads one to presume that the process may involve the transfer of an electron from the nitrite ion to the

diazonium cation resulting in the generation of a phenyl radical via the formation of a diazenyl radical. Subsequent dimerization of phenyl radicals would yield biphenyl.

The reactions of arenediazonium salts with sodium nitrite in aqueous solutions, in the absence of a catalyst are known⁸⁹ to yield nitroaromatics in 10-75% yields. The mechanism proposed⁸⁹ for these reactions is given in Scheme III.11:

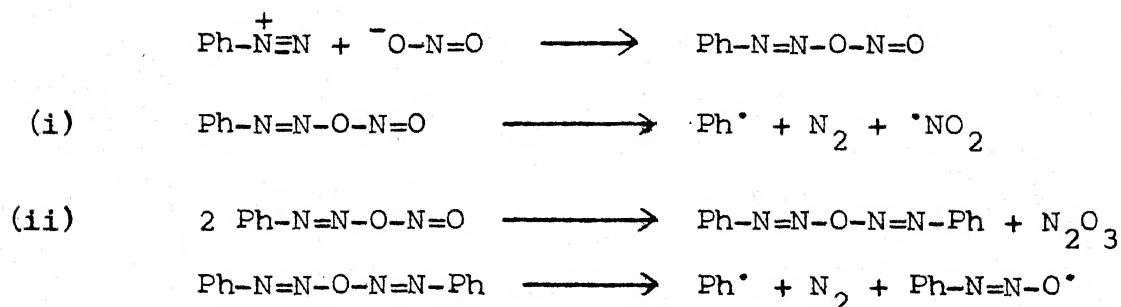
SCHEME III.11



(X = any substituent and n = an integer).

The orientation and partial rate factors for the phenylation of substituted benzenes with benzenediazonium tetrafluoroborate and sodium nitrite in DMSO have been studied⁸⁸ and based on the data obtained, intervention of phenyl radicals in these reactions has been suggested.⁹⁰⁻⁹² Two alternative modes of formation of phenyl radicals, which have been considered,⁹⁰ are outlined in Scheme III.12:

SCHEME III.12



In view of the interesting mechanistic possibilities of reactions of ambident nucleophiles at various electrophilic sites in arenediazonium cations, it was decided to examine the reactions of some arenediazonium cations with nitrite and 2-nitropropanate anions.

III.3 Results and Discussion

The occurrence of a novel electron transfer mechanism involving free radical intermediates in the reactions of arenediazonium cations with the iodide ion was reported some time back from our laboratory.^{65,66} It is also known⁸⁸ that reactive aryl radicals are formed as intermediates in the reactions of arenediazonium salts with the ambident nitrite anion; but the mode of formation of these aryl radicals is not clear.⁸⁹ The reactions of another useful, ambident nucleophile, 2-nitropropan-2-ide (which is a potential electron donor towards positively charged substrates) with arenediazonium cations have not yet been reported in the literature. It was, therefore, decided to examine the mechanistic details of the reactions of a few arenediazonium salts with ambident nitrite and 2-nitropropan-2-ide anions.

The reactions of benzenediazonium fluoroborate Ia, p-nitrobenzenediazonium fluoroborate Ib, and p-methoxybenzenediazonium fluoroborate Ic, with sodium nitrite in methanol medium at 0°C, under varying conditions gave the results summarized in

Table III.1. From the data obtained, it is clear that in comparison to the reference substituent H, the electron withdrawing $p\text{-NO}_2$ group in the aromatic ring of the arenediazonium salt accelerates, while the electron donating $p\text{-CH}_3\text{O}$ group retards the reaction. This rules out the possibility of aryl cation intermediates in these reactions, the formation of which would require rate retardation with both the $p\text{-NO}_2$ and $p\text{-CH}_3\text{O}$ substituents.⁹⁸ Sensitivity to photochemical catalysis, as evident from the observed difference in the speeds of the reaction in the presence and absence of light, rules out the possibility of a simple nucleophilic displacement of nitrogen.⁹⁹ This mechanism would also not explain the formation of formaldehyde, protodediazoniated products and biaryls actually obtained in these reactions. Our inability to detect any *m*-dinitrobenzene among the products in the reaction of *p*-nitrobenzenediazonium fluoroborate, and *m*-nitroanisole amongst the products in the reaction of *p*-methoxybenzenediazonium fluoroborate, in spite of careful search, clearly eliminates the possibility of occurrence of an elimination-addition mechanism (involving aryne intermediates) in these reactions. The reaction of benzenediazonium fluoroborate with sodium nitrite, when conducted in the presence of acrylonitrile under nitrogen atmosphere yielded polyacrylonitrile, as observed by Beringer and Bodlaender¹⁰⁰ in the free radical reactions of arylidonium salts with titanous chloride. The reactions of benzenediazonium fluoroborate and *p*-nitrobenzenediazonium fluoroborate with NaNO_2 were found to be inhibited in the presence of molecular oxygen (runs 3 and 8).

TABLE III.1: Reactions^a of Arenediazonium Fluoroborates I with Sodium Nitrite in Methanol at 0°C.

Run	Arene-diazonium Fluoroborate <u>I</u>	Molar Ratio $\text{NaNO}_2:\text{I}$	Reaction Atmosphere	% Yield of Products ^b					
				Nitrogen	$\text{R-C}_6\text{H}_5$	$\text{p-R-C}_6\text{H}_4\text{NO}_2$	$\text{p-R-C}_6\text{H}_4\text{OH}$	Biaryls	CH_2O ^c
1	<u>Ia</u>	1.00	Nitrogen	100% in 600 sec.	44	13	5	21	35
2	<u>Ia</u>	0.75	Nitrogen	90% in 600 sec.	42	9	4	18	34
3	<u>Ia</u>	1.00	Oxygen ^d	51% in 1800 sec.	11	4	22	5	10
4 ^e	<u>Ia</u>	1.00	Nitrogen	100% in 1200 sec.	45	12	5	20	37
5 ^f	<u>Ia</u>	1.00	Nitrogen	100% in 300 sec.	48	10	3	26	40
6	<u>Ib</u>	1.00	Nitrogen	100% in 120 sec.	60	12	4	16	51
7	<u>Ib</u>	0.75	Nitrogen	100% in 120 sec.	68	8	2	14	57
8	<u>Ib</u>	1.00	Oxygen ^d	80% in 1800 sec.	41	6	21	7	40
9 ^g	<u>Ic</u>	1.00	Nitrogen	10% in 3600 sec.	8	-	-	-	5

a, 5×10^{-3} mol of $\text{p-R-C}_6\text{H}_4\text{-N}_2^+\text{BF}_4^-$ were reacted with NaNO_2 in methanol solvent at 0°C.

b, Percentages based on arenediazonium fluoroborate.

c, Estimated as dimedone derivative.

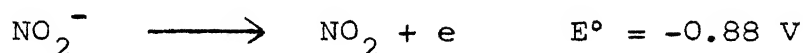
d, Initial oxygen atmosphere was gradually replaced by nitrogen as reaction proceeded.

e, In dark; f, In the presence of 5×10^{-5} mol of CuBr_2 .

g, On the addition of diethyl ether, 90% of Ic was recovered back.

These observations indicate that aryl radicals may be effective intermediates in the reactions under consideration. Indeed, generation of phenyl radicals by the reaction of nitrite ion with benzenediazonium salts in DMSO has been reported to constitute the best preparative method towards homolytic aromatic phenylation.⁸⁸ The intermediacy of covalent, kinetically controlled products (see ref. 117) i.e., diazonitrites,^{91,92} which could produce radical species by the homolysis of C-N and N-O bonds, is unlikely in these reactions, in view of the observation that in the reaction of p-methoxybenzenediazonium fluoroborate, 80% of the starting material was recovered unchanged on addition of diethyl ether to the reaction mixture after 3600 sec. On the other hand, the ambident 2-nitropropanate anion was found to react with p-methoxybenzenediazonium cation at 0°C in methanol medium to yield the thermodynamically stable (see ref. 117) p-methoxybenzeneazo-2-(2-nitro)propane in 85% yield (cf. Table III.2). These observations highlight the fact that the formation of azo compounds in the reactions of I_c with some anions other than nitrite anion is a facile process at 0°C. It is noticed that the kinetically controlled product i.e. the diazonitronic ester was not formed in this reaction (see discussion later in this section). Also, the substantial difference in rates observed in the reactions of benzenediazonium fluoroborate and p-methoxybenzenediazonium fluoroborate is inconsistent with the difference in rates expected in such cation-anion reactions of arenediazonium salts.¹⁰¹ Furthermore, the time for 100%

completion of the reaction of p-nitrobenzenediazonium fluoro-borate with sodium nitrite taken in 1:0.75 molar ratio (run 7) is the same as for the two reactants taken in equimolar ratio. If the diazonitrite intermediate was involved then the two reactants in 1:0.75 molar ratio could not have given more than 75% reaction. It is noteworthy in this context that nitrite ion has a redox potential¹⁰² much less than the reported⁵¹ threshold redox potential of 1 V for the reductants in the one electron transfer reduction of arenediazonium cations.

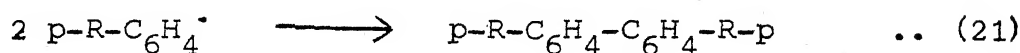
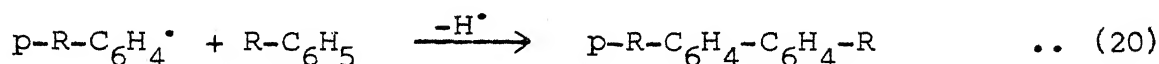
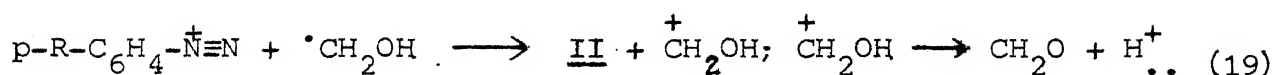
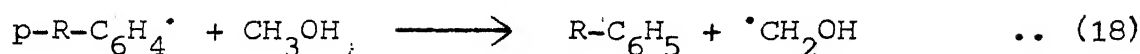
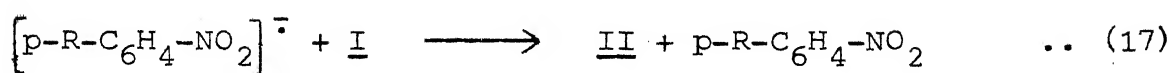
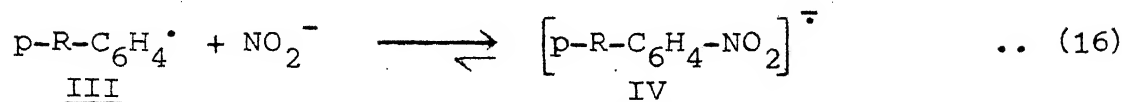
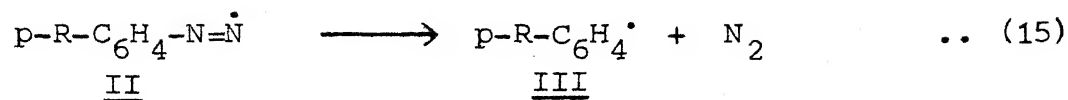
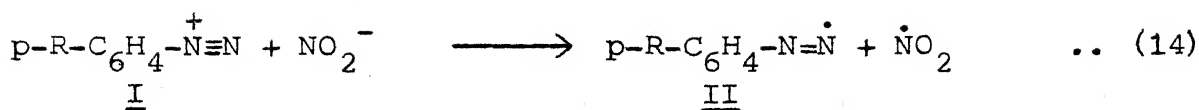


Nitrite ion is also known^{96,97} to reduce oxidizing agents known to be comparatively weaker than the arenediazonium cations. The arenediazonium cations on the other hand, are known⁶⁸ to undergo reduction by accepting an electron in the π system.

In view of the foregoing observations and arguments, we propose an electron transfer chain mechanism outlined in Scheme III.13, which accounts for all the observations recorded for our reactions of arenediazonium cations with the nitrite anion.

The initiation step is a photochemically catalyzed single electron transfer from the nitrite ion to the LUMO of the arenediazonium cation I, through the formation of a π -complex. The diazenyl radical II, may undergo heterolysis of the C-N bond to yield gaseous nitrogen and an electrophilic π -aryl radical.⁶⁵

SCHEME III.13

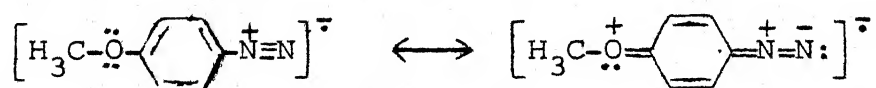


This electrophilic π -aryl radical reflects the nature of the transition state leading to it and may at best have a transitory existence before reverting to the stable σ -aryl radical. The σ -phenyl radical III is more stable by 2.45 eV, than the π -phenyl radical.¹⁰³ The σ -aryl radical so formed, may then couple with the ambident nitrite anion to yield the radical anion IV.

The σ -aryl radical has one electron in a carbon sp^2 orbital, the axis of which is in the plane of the benzene ring. Conceivably, as the filled lone pair orbital of the nitrogen atom in the

nitrite anion overlaps with the partially vacant sp^2 orbital of the aryl radical to form a σ bond, the "extra" electron is accommodated in the σ^* orbital of the C-N bond under formation. The immediate product of such a combination of a radical and an anion is thus a σ^* radical anion.¹⁰⁴ The σ^* radical anion then changes slowly into the more stable π^* radical anion, presumably with the assistance of bending vibrations to circumvent the orthogonality constraint. The C-N σ^* (antibonding) orbital is at a high energy level owing to the high electronegativity of nitrogen and thus, the energy requirement for the C-N coupling reaction would be high.¹⁰⁵ This energy requirement is effectively satisfied by the formation of the new C-N σ bond in the radical anion.

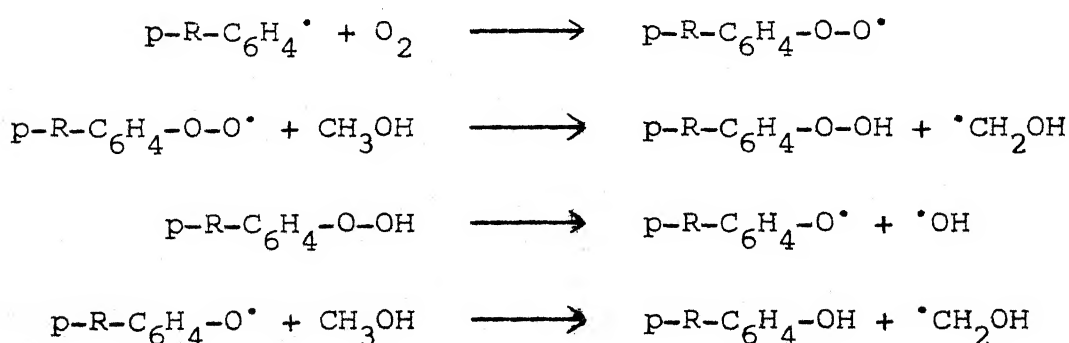
The π^* radical anion IV then transfers an electron to the arenediazonium cation I by a $\pi^* \rightarrow \pi^*$ electron transfer⁶⁸ process, propagating the chain. The chain termination occurs via steps (18), (20) and (21). Owing to high energy requirements of step (16) and good hydrogen atom donating ability of methanol, step (18) is faster than step (16), resulting in lower yields of nitrated products as compared to protodediazoniated products.¹⁰⁶ The reaction with $p\text{-CH}_3\text{O-C}_6\text{H}_4\text{-N}_2^+$ is, however, slower due to its lower oxidizing power^{52b} (in terms of half wave potentials) compared to $\text{C}_6\text{H}_5\text{-N}_2^+$ or $p\text{-O}_2\text{N-C}_6\text{H}_4\text{-N}_2^+$, and also because of slower heterolysis^{53, 65} of the C-N bond in $[p\text{-CH}_3\text{O-C}_6\text{H}_4\text{-N}_2^+]^-$.



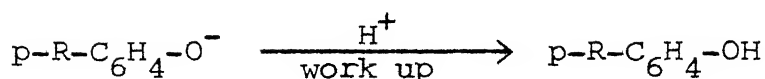
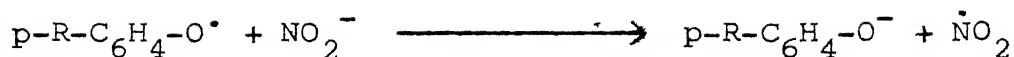
The fact that p-methoxyphenyl radical does not couple with the nitrite anion,¹⁰⁷ due to its lower electrophilicity, explains the total absence of p-methoxynitrobenzene among the products in run 9.

Oxygen inhibits the reaction presumably by interfering with the chain process^{108,109} of Scheme III.13. It is known¹¹⁰ that molecular oxygen rapidly reacts with the potassium salt of nitrobenzene radical anion to give potassium superoxide $K^+O_2^-$ and nitrobenzene quantitatively. We, therefore, suggest that oxygen can effectively interrupt the chain process by accepting an electron from the radical anion IV. Oxygen may also couple with the aryl radicals to produce an aryl hydroperoxide¹⁸ which decomposes to give an aryloxyradical.¹¹¹ This aryloxy radical may abstract a hydrogen atom from methanol to yield phenol¹¹² as outlined in Scheme III.14:

SCHEME III.14

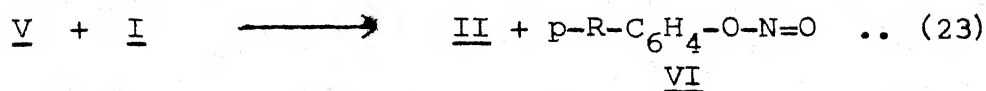
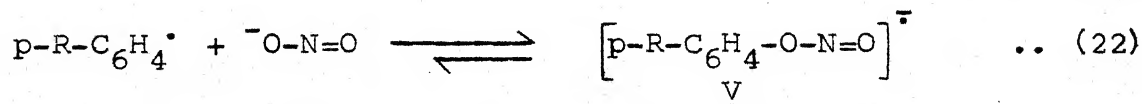


Alternatively, the aryloxy radical may accept an electron from the nitrite ion to give aryloxy anion, which may yield phenol on work up.

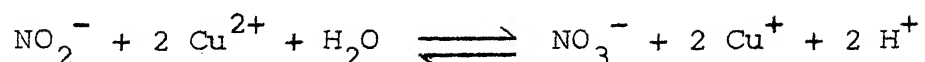


Steps (16), (18), (19) and (20) of the Scheme III.13 are preceded. ^{60a, 113, 114}

Phenols, formed in small amounts in the reactions of benzenediazonium fluoroborate Ia and p-nitrobenzenediazonium fluoroborate Ib with sodium nitrite under nitrogen atmosphere, do not arise due to the presence of oxygen as impurity in the nitrogen gas sample used, since the reaction of Ia with cuprous bromide using the same batch of nitrogen does not produce even a small quantity of phenol. Cuprous ions are known to generate aryl radicals on reaction with arenediazonium cations.⁵¹ Also, since arenediazonium cations I were found to be stable in methanol under our reaction conditions and did not decompose to yield methyl aryl ethers even in traces on stirring for 2 hours in methanol at 0°C, the possibility of formation of aryl cations is ruled out.²⁷ An alternative conceivable pathway is the coupling of aryl radicals through the oxygen atom of the ambident nitrite anion, to yield the radical anion V. This radical anion V could transfer an electron to arenediazonium cation I, yielding the nitrite VI:



completion. In aqueous solutions, nitrite ion is known¹¹⁵ to reduce cupric salts to cuprous salts, as shown below:



This cuprous ion then transfers an electron easily to the arene-diazonium cation, thereby accelerating the reaction. The fact that a catalytic amount of CuBr_2 considerably reduces the reaction time, indicates that we are dealing with an oxidation reduction system.

The reactions of benzenediazonium fluoroborate Ia, p-nitrobenzenediazonium fluoroborate Ib, and p-methoxybenzenediazonium fluoroborate Ic, with lithium 2-nitropropan-2-ide in methanol at 0°C, under varying conditions, gave the results summarized in Table III.2. It is noteworthy that the reactions of benzenediazonium fluoroborate and p-methoxybenzenediazonium fluoroborate with 2-nitropropanate anion, yield the corresponding azo compounds namely, benzeneazo-2-(2-nitro)propane and p-methoxybenzeneazo-2-(2-nitro)propane, respectively, in near quantitative yields. Since the 2-nitropropanate anion has most of its negative charge on oxygen atoms, in its planar most stable conformation,¹¹⁶ it is expected to couple with arenediazonium cations through its oxygen atom, if a simplified cation-anion interaction is postulated. Such an unstable intermediate would decompose by the N-O bond homolysis,⁹⁰ at higher temperatures, yielding the diazenyl radical, 2-nitropropyl radical and molecular nitrogen as shown in Scheme III.15:

TABLE III.2: Reactions^a of Arenediazonium Fluoroborates I, with Lithium 2-Nitropropan-2-ide in Methanol at 0°C.

Run	Arene-diazonium Fluoroborate <u>I</u>	Reaction Atmosphere	% Yield of Products ^b					
			Nitrogen	R-C ₆ H ₅	p-R-C ₆ H ₄ -CMe ₂ NO ₂	p-R-C ₆ H ₄ -C ₆ H ₄ -R (Isomeric mixture)	CH ₂ O ^c	p-R-C ₆ H ₄ -N=N- O ₂ NMe ₂ C
1	<u>Ia</u>	Nitrogen	-	-	-	-	-	90
2 ^d	<u>Ia</u>	Nitrogen	35	18	10	3	15	54
3	<u>Ib</u>	Nitrogen	40	32	4	2	27	45 ^e
4 ^f	<u>Ib</u>	Oxygen	20	3	tr	-	-	67
5 ^d	<u>Ib</u>	Nitrogen	54	43	5	3	36	35
6	<u>Ic</u>	Nitrogen	-	-	-	-	-	85
7 ^d	<u>Ic</u>	Nitrogen	26	20	5	tr	17	51

a, 5×10^{-3} mol of arenediazonium fluoroborate was reacted with equimolar amount of lithium 2-nitropropan-2-ide in methanol at 0°C under nitrogen atmosphere, unless otherwise stated.

b, Percentages based on arenediazonium fluoroborates. In addition p-nitrophenol (14%) was also formed in run 4.

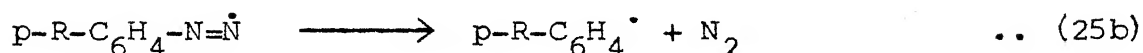
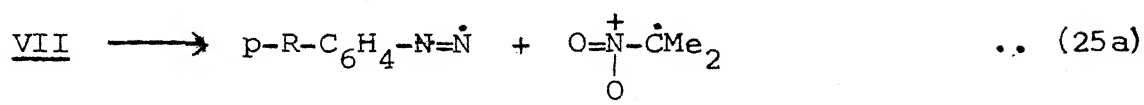
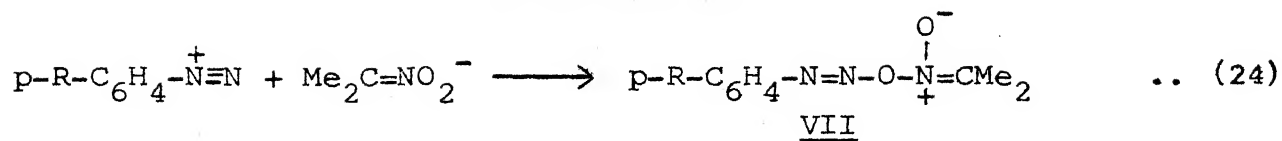
c, Estimated as dimedone derivative.

d, In the presence of 5×10^{-4} mol of cuprous bromide.

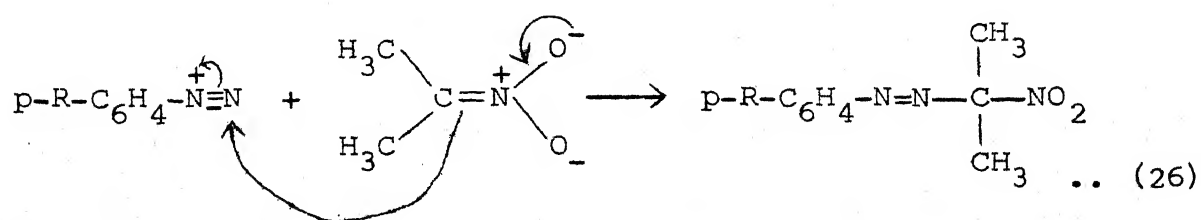
e, The p-nitrobenzeneazo-2-(2-nitro)propane was observed to be stable under our reaction conditions. 5×10^{-3} mol of p-nitrobenzeneazo-2-(2-nitro)propane was stirred in 30 ml methanol at 0°C for 3 hr. On subsequent work up, the starting azo compound was recovered back quantitatively by column chromatography of the reaction mixture.

f, Initial oxygen atmosphere was gradually replaced by nitrogen as reaction proceeded.

SCHEME III.15

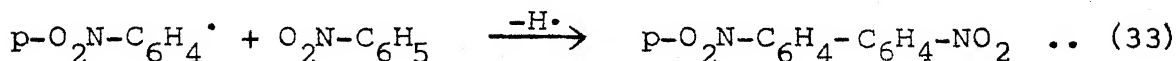
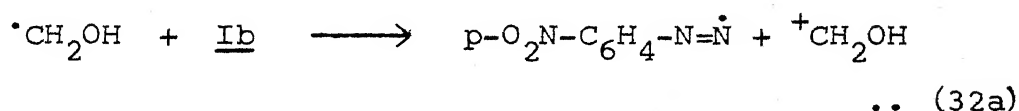
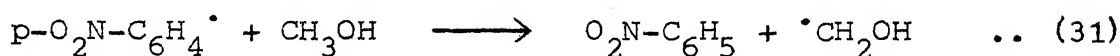
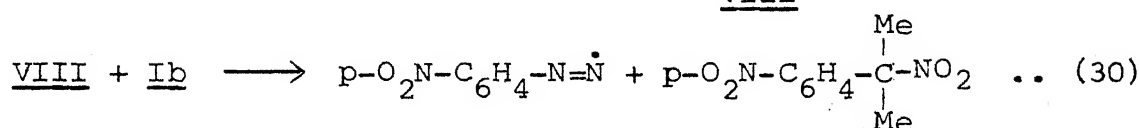
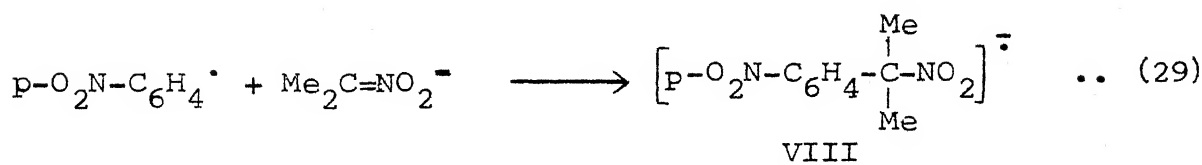
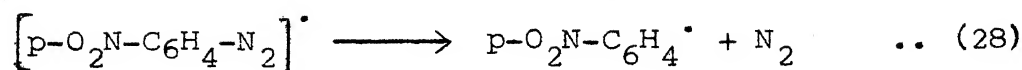
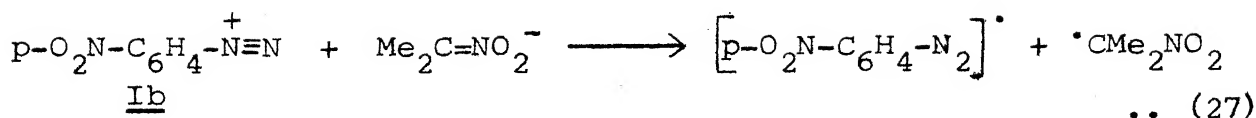


Formation of such an intermediate, in our reactions, is ruled out since nitrogen gas was not evolved in the reaction of benzenediazonium fluoroborate even on warming the reaction mixture from 0°C to room temperature. This observation coupled with the fact that the staggered pyramidalized conformation of 2-nitropropanate anion, with negative charge concentrated on the carbon atom, has a very high energy (+43 kcal/mol) and accordingly a very low probability of occurrence,¹¹⁶ lead us to conclude that the formation of azo compounds in this reaction of arenediazonium cations occurs via an electrophilic attack of the beta-nitrogen of arenediazonium cation on the central carbon atom of 2-nitropropanate anion as shown in Eqn. 26:



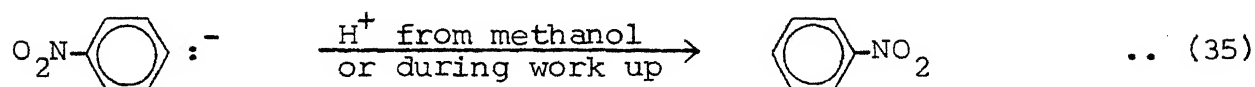
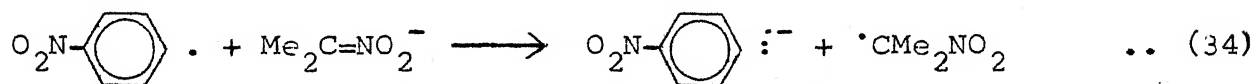
The formation of intermediate VII may be hindered by the high degree of solvation of highly electronegative oxygen atoms of 2-nitropropanate anion by the protic methanol solvent.¹¹⁷

SCHEME III.16



The p-nitrodiazenyl radical, $\text{p-O}_2\text{NC}_6\text{H}_4\text{N}=\overset{\cdot}{\text{N}}$ formed in step 27, decomposes by a heterolytic cleavage of the C-N bond, yielding gaseous nitrogen and a stable σ -p-nitrophenyl radical via an electrophilic π -p-nitrophenyl radical.⁶⁵ This σ -p-nitrophenyl radical may couple with the 2-nitropropanate anion to yield the radical anion VIII, which transfers an electron to the p-nitrobenzenediazonium cation by a $\pi^* \rightarrow \pi^*$ electron transfer process.⁶⁸ The p-nitrophenyl radical may also abstract a hydrogen

atom from methanol to yield nitrobenzene¹¹³ (step 31) or attack the initially formed nitrobenzene¹¹⁴ to yield a mixture of isomeric dinitrobiphenyls (step 33). The formation of significant amounts of nitrobenzene in this reaction, highlights the effectiveness of the chain termination¹⁰⁶ (step 31). The p-nitrophenyl radical itself is a good single electron oxidant and may accept an electron from the 2-nitropropanate anion giving p-nitrophenyl anion,¹⁰⁷ which may subsequently produce nitrobenzene on work up or by abstracting a proton from the solvent (Eqns. 34 and 35), thus contributing to chain termination:

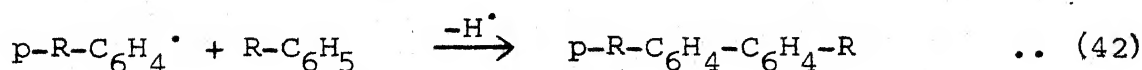
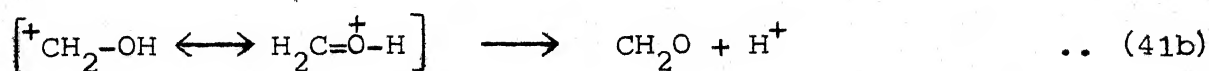
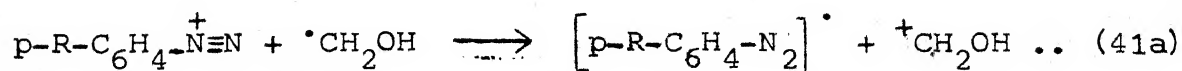
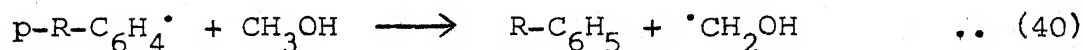
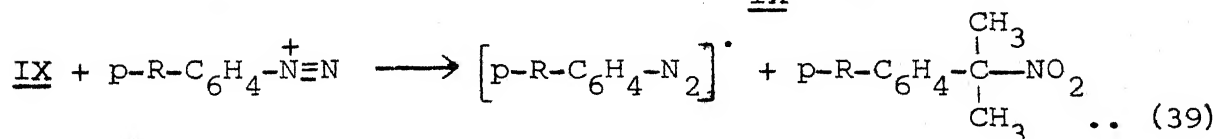
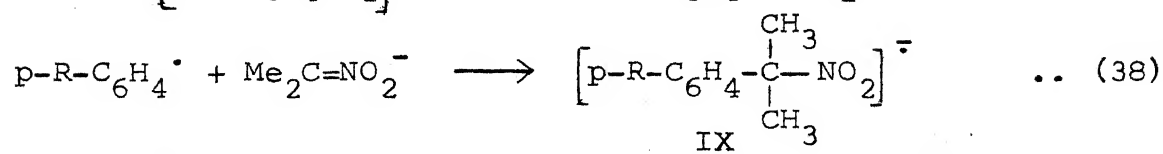
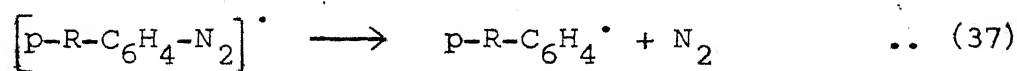
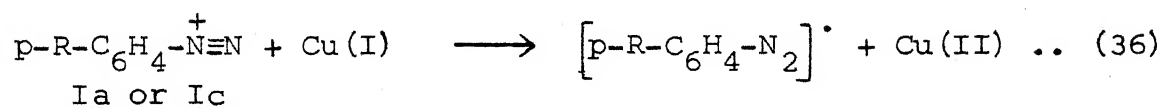


Coupling of the p-nitrophenyl radical through the oxygen atom of 2-nitropropanate anion does not occur, due to a large difference in the electronegativities of carbon and oxygen. Thus, the radical anion expected to form by such a C-O coupling would have a very high energy σ^* orbital compared to the π^* orbital of the radical anion formed by the C-C coupling,¹⁰⁴ as discussed earlier. Oxygen inhibits^{108,109} the reaction presumably by scavenging the aryl radicals and interfering with step 30.

Due to the lower reduction potentials^{52b} of benzenediazonium cation and the p-methoxybenzenediazonium cation, the

2-nitropropanate anion is unable to reduce them by the transfer of an electron in the manner discussed above. Consequently, only the azo coupling reaction is observed. Indeed, we observed that in the presence of 10 % mol of highly reducing cuprous bromide⁵¹ catalyst, the 2-nitropropanate anion reacts even with benzenediazonium fluoroborate and p-methoxybenzenediazonium fluoroborate to produce nitrogen gas. The amount of nitrogen gas evolved with the attendant dediazonation reaction is much larger than expected from the electron transfer reduction of arenediazonium cations by Cu(I). Thus, an induced S_{RN}1 process, termed as entrainment process,^{93,119} outlined in Scheme III.17, is visualized to account for all the observations recorded for these reactions (runs 2 and 7):

SCHEME III.17



The aryl radicals formed in step 37, couple¹⁰⁷ with the 2-nitropropanate anion to yield the radical anion IX, which subsequently transfers an electron to the arenediazonium cation Ia or Ic, propagating the chain. Owing to the high reactivity and poor selectivity of aryl radicals,¹²⁰ the termination of the chain by step 40 occurs very effectively. This is also supported by the fact that the reaction of p-nitrobenzenediazonium fluoroborate is not markedly influenced by the addition of 10% mol of cuprous bromide with the 2-nitropropanate anion.

III.4 Experimental

All melting points were taken on MEL-TEMP melting point apparatus. IR spectra were recorded on Perkin-Elmer, model-580 infrared spectrophotometer. GLC analyses were carried out on a Chromatography and Company model AC1-FI chromatograph using 10% SE-30 on Crom-P (85-100 M) column of 2 m length. Column chromatography was done over activated silica gel (100-200 M). Silica-gel (asc-India) was used for TLC analyses. Reaction products were identified by comparison of their retention times in GLC, IR Spectra and TLC with those of the authentic samples, elemental analyses, melting or boiling points and mixed melting points. Literature melting or boiling points are cited from "Handbook of Chemistry and Physics," 50th edition, R.C. Weast (Ed.) published by the Chemical Rubber Company, Cleaveland, Ohio, unless otherwise specified.

Starting Materials

Benzenediazonium fluoroborate, p-nitrobenzenediazonium fluoroborate and p-methoxybenzenediazonium fluoroborate were prepared by known¹²¹ procedures and purified before use by dissolving in acetone followed by precipitation by the addition of absolute ether. Sodium nitrite (BDH) was dried at 60°C for 3 hr before use. Lithium 2-nitropropan-2-ide was prepared by the known procedure.¹²² Absolute methanol¹²³ was deaerated by bubbling pure dry nitrogen gas through it for an hour and stored in a sealed flat bottomed flask. Cuprous bromide was prepared by the known¹²³ procedure and used immediately. Dimedone (BDH) was used without further purification.

Stability of arenediazonium fluoroborates in methanol at 0°C

A slurry of benzenediazonium fluoroborate (0.96 g, 5×10^{-3} mol) in deaerated dry methanol (60 ml) taken in a 250 ml 3-neck flask, fitted with a reflux condenser, connected to a mercury trap, and maintained at 0°C, was flushed with pure dry nitrogen gas under magnetic stirring for 30 min. Stirring was continued for further 2 hr, but no evolution of nitrogen was observed. On removal of the solvent, benzenediazonium fluoroborate was quantitatively recovered by adding dry ether to the conc. methanol slurry. Similarly, p-nitrobenzenediazonium fluoroborate and p-methoxybenzenediazonium fluoroborate were also found to be stable at 0°C. Not even a trace of aryl methyl ethers could be detected (GLC) in the recovered materials from any of the three experiments.

1. Reactions of benzenediazonium fluoroborate Ia with sodium nitrite at 0°C

(a) Reaction with equimolar quantity of Ia and NaNO_2 , under nitrogen atmosphere in ordinary laboratory light

In a 3-neck 250 ml round bottom flask mounted over a magnetic stirring base, with a magnet inside, and connected to a nitrogen gas cylinder through a purifier, to a gas collector through a mercury trap and to a pressure equalizing dropping funnel was placed a slurry of benzenediazonium fluoroborate (0.96 g; 5×10^{-3} mol) in 30 ml deaerated methanol. The contents of the flask were cooled to 0°C with ice-bath and the temperature maintained throughout the reaction period. The solution was purged with nitrogen gas with stirring, for 30 min, and then the supply of nitrogen gas from the cylinder was discontinued. A solution of sodium nitrite (0.345 g; 5×10^{-3} mol) in 30 ml deaerated methanol was added through the dropping funnel, with continuous stirring. The reaction started spontaneously with evolution of nitrogen gas and the color of the reaction mixture changed to reddish brown. The reaction was complete in 600 sec. as determined by the quantitative evolution of the nitrogen gas (112 ml as at NTP). Thereafter, the mixture was poured into 350 ml of distilled water and the total volume made upto 500 ml by the addition of distilled water. A 100 ml portion of this solution was kept aside for the determination of formaldehyde and the remaining solution extracted with five 50 ml portions of ether. The combined ethereal extract was washed, dried

(anhydrous MgSO_4), filtered and carefully concentrated at reduced pressure and room temperature to a volume of 50 ml. This was analyzed by GLC using 10% SE-30 on Crom-P (85-100 M) column of 2 m length. Products were identified by comparison of their retention times with those of the authentic samples. Yields of the products were estimated by comparison of peak areas with those from equal aliquots of standard solutions of authentic samples in ether. The yields of various products were estimated to be: benzene (44%), phenol (5%), nitrobenzene (13%) and biphenyl (21%).

Determination of Formaldehyde

To the 100 ml solution kept for the determination of formaldehyde, 100 ml of an aqueous solution of methone was added. After stirring for 6 hr, the mixture was allowed to stand for 40 hr. The precipitated dimedone derivative of formaldehyde was separated by filtration and dried at 60°C . The yield of this derivative corresponded to a total of 35% of formaldehyde formed in this reaction. The derivative was characterized by mixed melting point and its superimposable IR spectrum with that of an authentic sample.

(b) Reaction with equimolar quantity of Ia and NaNO_2 in initial oxygen atmosphere under ordinary laboratory lights

Dry oxygen gas was bubbled for 30 minutes through a slurry of benzenediazonium fluoroborate (0.96 g; 5×10^{-3} mol) in 30 ml methanol kept in the reaction flask at 0°C . All other conditions

were the same as described for the reaction 1(a). A solution of sodium nitrite (0.345 g; 5×10^{-3} mol) in 30 ml methanol was added to the above slurry of the diazonium salt. Nitrogen gas corresponding to 51% (57 ml as at NTP) completion of the reaction was evolved in 1800 sec. The reaction mixture was worked up and the products analyzed as described for the reaction 1(a) above. The product distribution was: benzene (11%), phenol (22%), nitrobenzene (4%) and biphenyl (5%). The yield of formaldehyde estimated as its dimedone derivative was 10%.

(c) Reaction with equimolar quantities of Ia and NaNO_2 , under nitrogen atmosphere in complete darkness

The reaction of benzenediazonium fluoroborate (0.96 g; 5×10^{-3} mol) taken in 30 ml methanol, with sodium nitrite (0.345 g; 5×10^{-3} mol) dissolved in 30 ml methanol was allowed to proceed at 0°C in complete darkness (the reaction flask was carefully wrapped in black paper), with rest of the reaction conditions remaining the same as in the reaction 1(a). The evolution of nitrogen gas was slower as compared to that in reaction 1(a) and it took 1200 sec. for the quantitative evolution of nitrogen (112 ml as at NTP). The reaction mixture was worked up and the products analyzed as described for the reaction 1(a). The product distribution was found to be: benzene (45%) phenol (5%), nitrobenzene (12%) and biphenyl (20%). The yield of formaldehyde estimated as its dimedone derivative was 37%. Benzenediazonium fluoroborate and methanol used in this reaction and the reaction 1(a) were taken from the same batch.

(d) Reaction of Ia with NaNO_2 in molar ratio 1:0.75, under nitrogen atmosphere and in ordinary laboratory lights

The reaction of benzenediazonium fluoroborate (0.96 g; 5×10^{-3} mol) with sodium nitrite (0.259 g; 3.75×10^{-3} mol) in methanol under nitrogen atmosphere at 0°C , with all the other reaction conditions remaining the same as for the reaction 1(a), was ca. 90% complete, as determined by the quantity of nitrogen gas evolved (101 ml as at NTP) in 600 sec. The reaction mixture, on work up as usual, yielded the product distribution: benzene (42%), phenol (4%), nitrobenzene (9%) and biphenyl (18%). The yield of formaldehyde estimated as its dimedone derivative was 34%.

(e) Reaction with equimolar amount of Ia and NaNO_2 , in nitrogen atmosphere under ordinary laboratory lights in the presence of cupric bromide

In a 3-neck flask, kept in an ice-bath (0°C) and mounted over a magnetic stirring base, a slurry of benzenediazonium fluoroborate (0.96 g; 5×10^{-3} mol) and cupric bromide (0.011 g; 5×10^{-5} mol) in deaerated methanol (30 ml) was taken. Pure and dry nitrogen gas was passed through the solution for 30 min. Stirring was started and a solution of sodium nitrite (0.345 g; 5×10^{-3} mol) in 30 ml deaerated methanol was added through a pressure equalizing dropping funnel. The reaction commenced immediately with a vigorous evolution of nitrogen gas and was complete in 300 sec., as observed by the quantitative evolution of nitrogen gas which was collected by the method of downward

displacement of water. The reaction was worked up as described for the reaction 1(a) and analyzed by GLC using 10% SE-30 on Crom-P (85-100 M) column of 2 m length. The yields of various products estimated were: benzene (48%), phenol (3%), nitrobenzene (10%) and biphenyl (26%). Formaldehyde, determined as its dimedone derivative, was found to be 40% (based on benzenediazonium fluoroborate).

(f) Reaction with equimolar amounts of Ia and NaNO_2 , in nitrogen atmosphere under ordinary laboratory lights, in the presence of acrylonitrile

The reaction of benzenediazonium fluoroborate (0.96 g; 5×10^{-3} mol) and 50 ml acrylonitrile taken in 30 ml methanol with sodium nitrite (0.345 g; 5×10^{-3} mol) contained in methanol (30 ml), at 0°C under nitrogen atmosphere, showed the formation of solid polyacrylonitrile after 30 min. After 3 hr, the solid was filtered and washed in turn with water, methanol and ether. It was recrystallized by dissolving in hot dimethylformamide and addition of water to the cold solution. The solid was filtered and dried, m.p. 260°C (dec); lit.¹⁰⁰ m.p. $250-310^\circ\text{C}$ (dec). Polyacrylonitrile was identified by its solubility characteristics and IR spectrum. The polymer was insoluble in water, alcohol, ethyl acetate, acetone, ether, dichloromethane and pentane but soluble in dimethylformamide. Characteristic infrared absorption bands at 2230 cm^{-1} (CN), 1450 cm^{-1} (CH, CH_2) and 1050 cm^{-1} (C-C skeletal) were observed as reported in the literature.¹⁰⁰

2. Reactions of p-nitrobenzenediazonium fluoroborate **Ib** with sodium nitrite at 0°C

(a) Reaction with equimolar amount of **Ib** and NaNO_2 under nitrogen atmosphere in ordinary laboratory lights

A slurry of p-nitrobenzenediazonium fluoroborate (1.185 g; 5×10^{-3} mol) in 30 ml methanol was allowed to react with a solution of sodium nitrite (0.345 g; 5×10^{-3} mol) in methanol (30 ml) at ice-bath temperature (0°C), under nitrogen atmosphere in an assembly described for the reaction 1(a). The reaction was 100% complete within 120 sec, as observed by the quantitative evolution of nitrogen gas. The reaction mixture was poured into 350 ml of distilled water and the total volume made up to 500 ml with distilled water. A 100 ml portion of this solution was immediately used for the estimation of formaldehyde and the remaining solution was extracted with ether (5 x 50 ml) in the usual manner. The combined ethereal extract was washed, dried (anhydrous MgSO_4), filtered and concentrated in the same manner as described for the reaction 1(a). The mixture of products was analyzed by GLC using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length. The products were identified by comparison of their retention times with those of the authentic samples and the yields were determined by comparing the peak areas with those from equal aliquots of standard solutions of authentic samples in ether. The yields of various products identified were: nitrobenzene (60%), p-nitrophenol (4%), and p-dinitrobenzene (12%). The crude mixture of products was concentrated

further and charged over a column of activated silica-gel (100-200 M). Elution with a mixture of petroleum ether (b.p. 60-80°C) and benzene in the ratio 4:1 first gave nitrobenzene (b.p. 85°/10 mm) in an yield comparable to that determined by GLC. Further elution of the column with a mixture of petroleum ether (b.p. 60-80°C) and benzene in the ratio 3:2, yielded p-dinitrobenzene (0.101 g; 12%). Subsequent elution with a mixture of petroleum ether (60-80°C) and benzene in the ratio 1:1 yielded a mixture of products, presumably a mixture of isomeric dinitrobiphenyls (0.098 g; ca. 16%). This last obtained mixture of dinitrobiphenyls gave a single spot on TLC and a single peak in GLC which coincided with the spot and peak for the authentic sample of 4,4'-dinitrobiphenyl. However, the melting point of this compound did not coincide with that of 4,4'-dinitrobiphenyl and furthermore, the mixed melting point of this compound with the authentic sample of 4,4'-dinitrobiphenyl, was depressed. Elemental analysis gave: C, 58.98; H, 3.21; N, 11.39%. Calculated for $C_{12}H_8N_2O_4$ (4,4'-dinitrobiphenyl or its isomers): C, 59.01; H, 3.28; N, 11.48%. Thus, it seems that the compound obtained is a mixture of isomeric dinitrobiphenyls, which are inseparable. The yield of formaldehyde isolated as its dimedone derivative was found to be 51%. GLC analysis showed the absence of m-dinitrobenzene in the reaction mixture.

(b) Reaction with equimolar amounts of Ib and $NaNO_2$ under initial oxygen atmosphere and ordinary laboratory lights

Dry oxygen gas was bubbled for 30 minutes through a slurry of p-nitrobenzenediazonium fluoroborate (1.185 g;

5×10^{-3} mol) in 30 ml methanol kept in a flask at 0°C . All other conditions were the same as described for the reaction 2(a). A solution of sodium nitrite (0.345 g; 5×10^{-3} mol) in 30 ml methanol was added to the above slurry of the arenediazonium salt. Nitrogen gas corresponding to 80% completion of the reaction was evolved in 1800 sec. The reaction mixture was worked up and the products analyzed by GLC and column chromatography as described for the reaction 2(a). The product distribution obtained was: nitrobenzene (41%), p-nitrophenol (21%), p-dinitrobenzene (6%) and a mixture of isomeric dinitrobiphenyls (0.025 g; ca. 7%). Yield of formaldehyde estimated as its dimedone derivative, was found to be 40%. GLC showed the absence of m-dinitrobenzene in the reaction mixture.

(c) Reaction of Ib with NaNO_2 in molar ratio 1:0.75, under nitrogen atmosphere, in ordinary laboratory lights

The reaction of p-nitrobenzenediazonium fluoroborate (1.185 g; 5×10^{-3} mol) with sodium nitrite (0.259 g; 3.75×10^{-3} mol) in methanol under nitrogen atmosphere at 0°C , with all the reaction conditions remaining the same as for the reaction 2(a), was 100% complete as determined by the quantitative evolution of nitrogen gas in 120 sec. (i.e. in the same time as required for the reaction 2(a)). This reaction mixture, on work up, and on analyses by GLC and column chromatography as detailed under the reaction 2(a), yielded the product distribution: nitrobenzene (68%), p-nitrophenol (2%), p-dinitrobenzene (8%) and a mixture

of isomeric dinitrobiphenyls (0.049 g; ca. 14%). The yield of formaldehyde, estimated as its dimedone derivative was 57%. GLC showed the absence of m-dinitrobenzene in the reaction mixture.

3. Reaction of p-methoxybenzenediazonium fluoroborate I_c , with an equimolar amount of sodium nitrite, under nitrogen atmosphere at 0°C, in ordinary laboratory lights

A slurry of p-methoxybenzenediazonium fluoroborate (1.11 g; 5×10^{-3} mol) in 30 ml methanol was allowed to react with a solution of sodium nitrite (0.345 g; 5×10^{-3} mol) in methanol (30 ml) at ice-bath temperature (0°C), under nitrogen atmosphere, in an assembly identical to that described for the reaction 1(a). The reaction was only 10% complete in 3600 sec, as observed by the volume of nitrogen gas evolved during this period. The reaction mixture, on work up and subsequent analyses by GLC as detailed under the reaction 1(a), yielded only anisole (8%). The yield of formaldehyde estimated as its dimedone derivative was 5%. m-Nitroanisole was not detected in the reaction mixture.

This reaction was repeated and after 3600 sec, 300 ml of ether was added to precipitate the unreacted p-methoxybenzenediazonium fluoroborate. The precipitate was filtered, washed with ether and dried. It was dissolved in acetone and precipitated out by the addition of ether. The yield of p-methoxybenzenediazonium fluoroborate recovered back was 0.887 g (80%).

4. Reaction of benzenediazonium fluoroborate Ia with an equimolar amount of cuprous bromide under nitrogen atmosphere at 0°C, in ordinary laboratory lights

Dry nitrogen gas, from the same batch as that used for the reaction Ia was passed for 30 min through a suspension of cuprous bromide (0.718 g; 5×10^{-3} mol) in deaerated methanol (30 ml) kept at 0°C, in an assembly identical to that described for the reaction 1(a). The mixture was stirred continuously and a slurry of benzenediazonium fluoroborate (0.96 g; 5×10^{-3} mol) in methanol (30 ml) was added with the help of a dropping funnel. The reaction was complete in 200 sec. as determined by the quantitative evolution of nitrogen gas. After 5 minutes, the reaction mixture was worked up as described for the reaction 1(a). The crude mixture of products was analyzed by GLC using 10% SE-30 on Crom-P (85-100M) column of 2 m length and the yields of various products estimated were: benzene (56%), bromobenzene (10%) and biphenyl (23%). Not even a trace of phenol could be detected in the reaction mixture. Formaldehyde, estimated as its dimedone derivative, was obtained in 55% yield.

5. Reactions of benzenediazonium fluoroborate, Ia, with lithium 2-nitropropan-2-ide at 0°C

(a) Reaction with equimolar amounts of Ia and lithium 2-nitropropan-2-ide under nitrogen atmosphere in ordinary laboratory lights

In a 3-neck, 250 ml round bottom flask mounted over a magnetic stirring base, with a magnet inside, and connected to a nitrogen gas cylinder through a purifier, to a gas collector through a mercury trap and to a pressure equalizing dropping

funnel was placed a slurry of benzenediazonium fluoroborate (0.96 g; 5×10^{-3} mol) in 30 ml deaerated methanol. The contents of the flask were cooled to 0°C with the help of an ice-bath and the temperature was maintained throughout the reaction period. The solution was purged with nitrogen gas for 30 min. The nitrogen cylinder was disconnected and a solution of lithium 2-nitropropan-2-ide (0.475 g; 5×10^{-3} mol) in 30 ml methanol was added through the dropping funnel, with continuous stirring. On addition, the solution turned light yellow, but no nitrogen gas was evolved. After 30 minutes, the solution turned dark yellow, but still no nitrogen gas evolved. The reaction mixture was poured into 350 ml of distilled water and extracted with five 50 ml portions of ether. The combined ethereal extract was washed, dried (anhydrous MgSO_4), filtered and carefully concentrated at reduced pressure and room temperature to a volume of 50 ml. GLC analysis of this material, did not show the presence of benzene, phenol, or biphenyl. It did not give a spot for 2-phenyl-2-nitropropane on TLC, on comparison with an authentic sample of the latter, but gave a spot for an unknown compound. The reaction mixture was further concentrated and was charged over a silica-gel (100-200 M) column. On elution with petroleum ether (b.p. $60-80^{\circ}\text{C}$) and benzene in the ratio of 3:1, a dark yellow oil (0.869 g) was obtained. Its IR spectrum (neat), Fig.III.1, showed a strong peak for NO_2 group (1550 cm^{-1}), C-N (851 cm^{-1}) and a doublet at 1380 and 1365 cm^{-1} for the gem-dimethyl groups. These observations as well as the results of elemental analysis confirmed this compound to be benzeneazo-2-(2-nitro)propane. Anal. C, 55.93; H, 5.65; N, 21.68%;

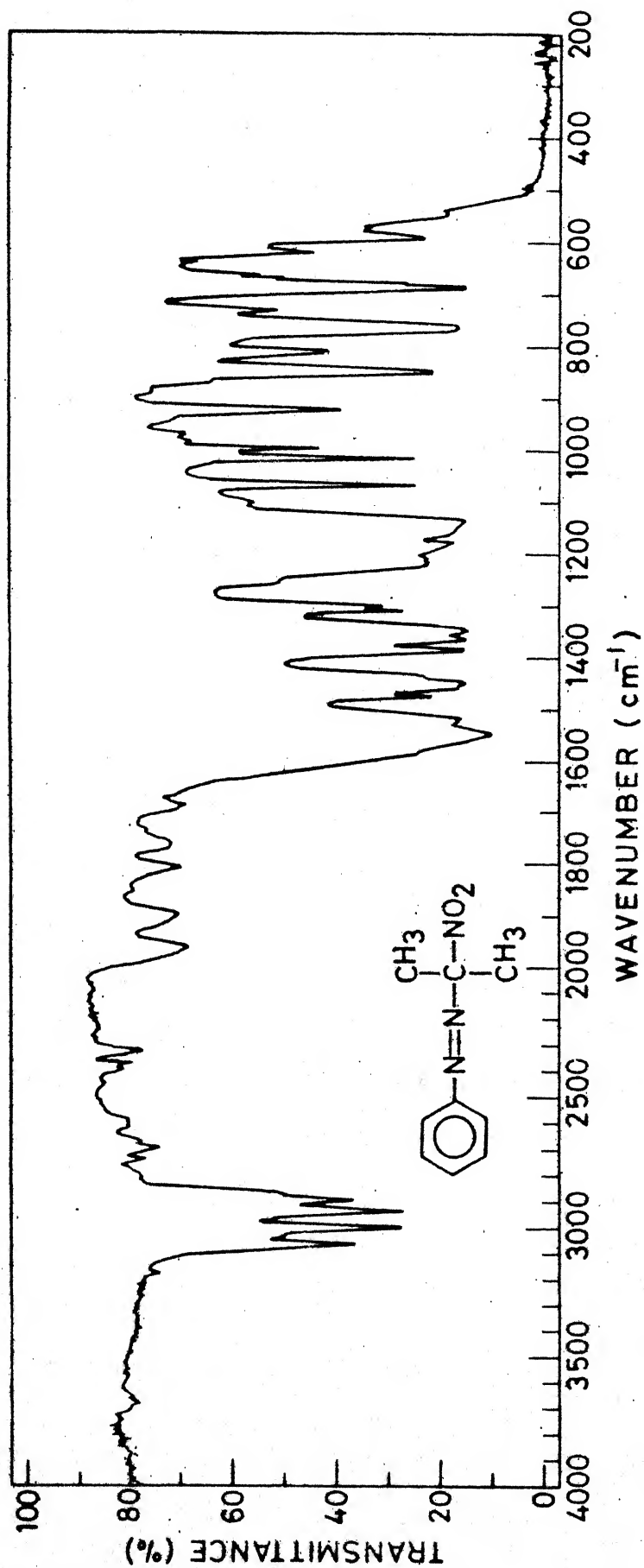


Fig. III.1 IR spectrum (neat) of Benzeneazo-2-(2-nitro) propane.

calculated for $C_9H_{11}N_3O_2$: C, 55.90; H, 5.70; N, 21.76%. Thus the percentage yield of the azo compound was 90%.

- (b) Reaction with equimolar amounts of Ia and lithium 2-nitropropan-2-ide in nitrogen atmosphere under ordinary laboratory lights, in the presence of cuprous bromide

In a 3-neck RB flask, kept at 0°C , a slurry of benzenediazonium fluoroborate (0.96 g; 5×10^{-3} mol) in deaerated methanol (30 ml) was taken. Dry nitrogen gas was passed through the solution for 30 min. Stirring was commenced and lithium 2-nitropropan-2-ide (0.475 g; 5×10^{-3} mol) and cuprous bromide (0.072 g; 5×10^{-4} mol) taken in 30 ml methanol was introduced through a pressure equalizing dropping funnel. The reaction commenced immediately with evolution of nitrogen gas. Nitrogen gas corresponding to 35% completion of the reaction was evolved in 15 min. Thereafter, no more nitrogen gas was evolved till 30 min. The reaction mixture was added to 350 ml of distilled water and the solution made upto 500 ml by the addition of distilled water. A 100 ml portion of this solution was immediately used for the determination of formaldehyde. The remaining solution was extracted with ether (5 x 50 ml) and the combined ethereal extract was washed, dried (anhydrous MgSO_4), filtered and concentrated under reduced pressure, to a volume of 50 ml. The mixture of crude products was analyzed by GLC using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length. The products were identified

by comparison of their retention times with those of the authentic samples, and the yields were determined by comparing the peak areas with those from equal aliquots of standard solutions of authentic samples in ether. The yields of various products identified were: benzene (18%) and biphenyl (3%). The reaction mixture was concentrated further and charged over a silica-gel (100-200 M) column. Elution of the column with petroleum ether (b.p. 60-80°C) and benzene in the ratio 3:1, first yielded 2-phenyl-2-nitropropane (0.083 g; ca. 10%), characterized by TLC analysis and comparison of its IR spectrum with that of an authentic sample. Further elution of the column with the same solvent yielded benzenediazo-2-(2-nitro)propane (0.522 g, 54%), characterized by its IR spectrum, which matched with the IR spectrum of this compound obtained in the previous experiment, and elemental analysis, which agreed with the composition of the proposed structure. Formaldehyde, characterized and estimated as its dimedone derivative, was found to be 15%.

(c) Reaction with equimolar amounts of Ia and lithium 2-nitropropan-2-ide under nitrogen atmosphere, in ordinary laboratory lights at 0°C followed by warming to room temperature

In a 3-neck RB flask kept in an ice-bath at 0°C, a slurry of benzenediazonium fluoroborate (0.96 g; 5×10^{-3} mol) in deaerated methanol (30 ml) was taken. After flushing the contents of the flask for 30 min with dry nitrogen, a solution of lithium 2-nitropropan-2-ide (0.475 g; 5×10^{-3} mol) in 30 ml

methanol was added through a pressure equalizing dropping funnel. On addition, the solution turned light yellow, but no nitrogen gas was evolved. After 30 min, the ice-bath was removed and the solution was allowed to warm up to the room temperature (30°C). No nitrogen gas was observed to evolve, even after stirring the reaction mixture for further 30 min. The reaction mixture was then worked up, as in the reaction 5(a) and analyzed by GLC and column chromatography. Benzene-azo-2-(2-nitro)propane was obtained in 90% yield (0.869 g). No other product could be identified. Benzeneazo-2-(2-nitro)-propane was characterized by its IR spectrum and elemental analysis.

6. Reactions of p-nitrobenzenediazonium fluoroborate Ib with lithium 2-nitropropan-2-ide at 0°C

(a) Reaction with equimolar amounts of Ib and lithium 2-nitropropan-2-ide in nitrogen atmosphere under ordinary laboratory lights

A slurry of p-nitrobenzenediazonium fluoroborate (1.185 g; 5×10^{-3} mol) in 30 ml methanol was allowed to react with a solution of lithium 2-nitropropan-2-ide (0.475 g; 5×10^{-3} mol) in methanol (30 ml) at ice-bath temperature (0°C), under nitrogen atmosphere, in an assembly identical to that described for the reaction 5(a). The reaction commenced with evolution of nitrogen gas and the solution turned orange yellow in color. Nitrogen gas corresponding to 40% completion of the reaction was

evolved in 30 min. The reaction mixture was worked up in the usual manner and analyzed by GLC using the calibration method. The yields of various products identified were: nitrobenzene (32%), α ,p-dinitrocumene (4%), and a mixture of isomeric dinitrobiphenyls (2%). The concentrated reaction mixture was then charged over a silica-gel (100-200 M) column. Elution of the column with a mixture of petroleum ether (b.p. 60-80°C) and benzene in the ratio 4:1, gave nitrobenzene (b.p. 85°/10 mm) in yield comparable to that determined by GLC analysis. Further elution of the column with a mixture of petroleum ether (b.p. 60-80°C) and benzene in the ratio 3:1 gave an orange yellow solid (0.536 g), m.p. 104-106°C. IR spectrum of this solid (KBr), Fig. III.2, showed a strong peak at 1545 cm^{-1} (NO_2) and a C-N stretching band at 848 cm^{-1} , besides a doublet at 1390 cm^{-1} and 1370 cm^{-1} (gem-dimethyl substituents). It showed one single band at 860 cm^{-1} , thus establishing that it is a p-disubstituted benzene. These observations combined with the results of elemental analysis proved this compound to be p-nitrobenzeneazo-2-(2-nitro)propane. Anal.: C, 45.78; H, 4.28; N, 23.15%; calculated for $\text{C}_9\text{H}_{10}\text{N}_4\text{O}_4$: C, 45.38; H, 4.20; N, 23.53%. Thus, the percentage yield of this azo compound (based on Ib) was 45%. Formaldehyde, estimated as its dimedone derivative was obtained in 27% yield.

(b) Reaction of Ib and lithium 2-nitropropan-2-ide, in equimolar ratio under initial oxygen atmosphere in ordinary laboratory lights

Dry oxygen gas was bubbled through a slurry of p-nitrobenzenediazonium fluoroborate (1.185 g; 5×10^{-3} mol) contained

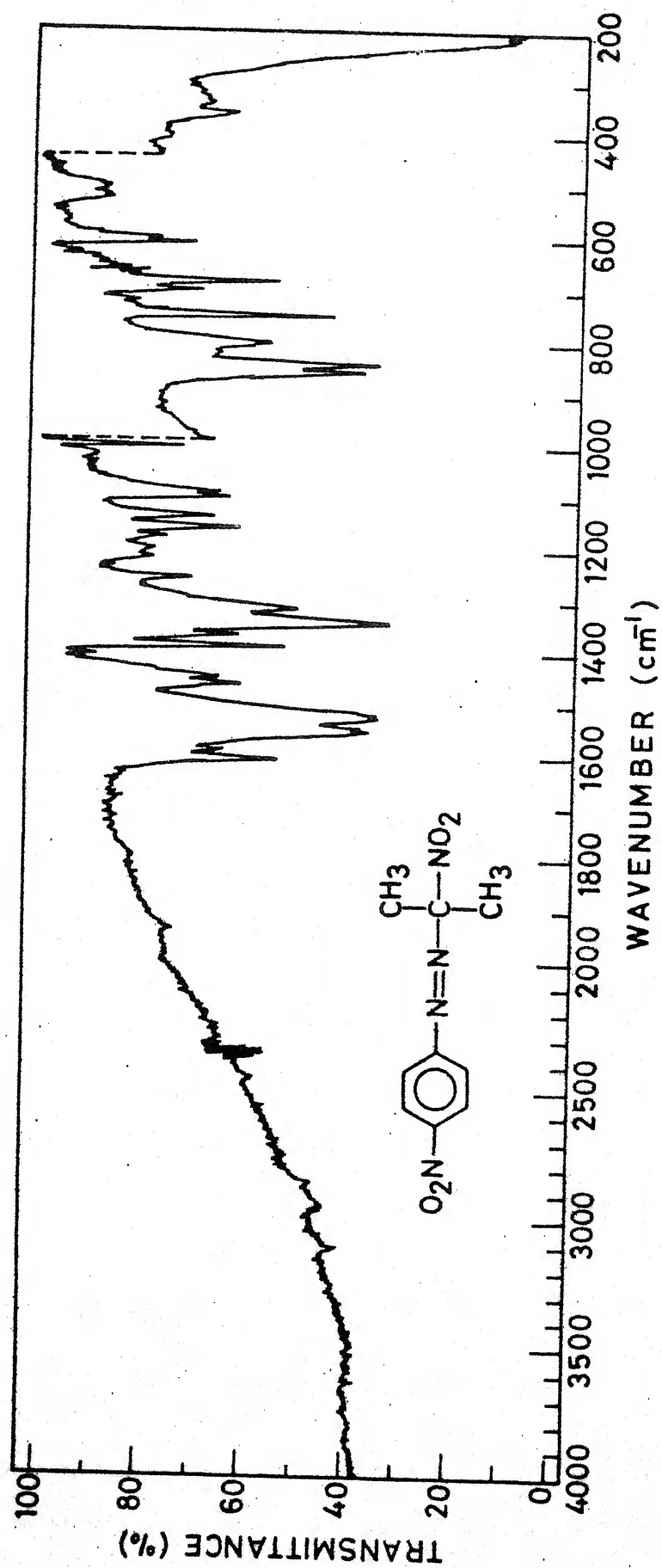


Fig. III. 2 IR spectrum of p-nitrobenzeneazo-2-(2-nitro)propane.

in 30 ml methanol and kept at 0°C. All other conditions were the same as described for the reaction 6(a). A solution of lithium 2-nitropropan-2-ide (0.475 g; 5×10^{-3} mol) in 30 ml methanol was added to the above slurry of arenediazonium salt. Nitrogen gas corresponding to 20% completion of the reaction was evolved in 30 min. The reaction mixture was work up and the products analyzed as described for the reaction 6(a). The product distribution was: nitrobenzene (3%), p-nitrophenol (14%), a trace of α ,p-dinitrocumene and p-nitrobenzeneazo-2-(2-nitro)-propane (0.797 g; 67%). The last mentioned compound was characterized by its IR spectrum and elemental analysis.

(c) Reaction of Ib and lithium 2-nitropropan-2-ide in equimolar ratio in nitrogen atmosphere under ordinary laboratory lights in the presence of cuprous bromide

A slurry of p-nitrobenzenediazonium fluoroborate (1.185 g; 5×10^{-3} mol) made in 30 ml methanol was reacted with lithium 2-nitropropan-2-ide (0.475 g; 5×10^{-3} mol) and cuprous bromide (0.072 g; 5×10^{-4} mol) taken in 30 ml methanol under nitrogen atmosphere. Rest of the reaction conditions were the same as in the reaction 6(a). Nitrogen gas (54%) was evolved in 15 min. The reaction mixture was stirred for further 15 min when no more nitrogen gas evolved, and then worked up as usual. Analysis of the crude mixture of products by GLC as described for the reaction 6(a) above, yielded nitrobenzene (43%), α ,p-dinitrocumene (5%) and a mixture of isomeric dinitrobiphenyls (3%). Column chromatography of the reaction mixture as described for

the reaction 6(a) yielded nitrobenzene (b.p. 85°/10 mm) in yield comparable to that determined by GLC, and p-nitrobenzeneazo-2-(2-nitro)propane (0.417 g; ca. 35%); m.p. 104°C. This compound was characterized by its IR spectrum (which matched with that obtained in the reaction 6(a)) and elemental analysis. Formaldehyde was obtained in 36% yield (estimated as its dimedone derivative).

- (7) Reactions of p-methoxybenzenediazonium fluoroborate I_c , with lithium 2-nitropropan-2-ide at 0°C
- (a) Reaction of I_c with lithium 2-nitropropan-2-ide in equimolar ratio under nitrogen atmosphere in ordinary laboratory lights

A slurry of p-methoxybenzenediazonium fluoroborate (1.11 g; 5×10^{-3} mol) in 30 ml methanol was allowed to react with a solution of lithium 2-nitropropan-2-ide (0.475 g; 5×10^{-3} mol) in methanol (30 ml) at ice-bath temperature (0°C), under nitrogen atmosphere in an assembly identical to that described for the reaction 5(a). On addition of the solution of 2-nitropropanate anion, the reaction mixture turned yellow in color; but no nitrogen gas was evolved. The reaction was worked up after 30 min, in the usual manner. GLC analyses of the product mixture did not give any peak for anisole, 2-(p-anisyl)-2-nitropropane or di-p-anisyl. The reaction mixture was charged over a column of silica gel (100-200 M). The column was eluted with a mixture of petroleum ether (b.p. 60-80°C) and benzene in the ratio 1:1. A light yellow solid (0.948 g), m.p. 94-96°C was obtained. The IR spectrum of

this solid (KBr), Fig. III.3 showed a strong band at 1550 cm^{-1} (NO_2), a doublet at 1360 cm^{-1} and 1370 cm^{-1} (gem-dimethyl substituents), another strong band at 1260 cm^{-1} (ether, C-O) and a band at 840 cm^{-1} (p-disubstituted benzene). These observations combined with the results of the elemental analysis proved this compound to be p-methoxybenzeneazo-2-(2-nitro)propane. Anal.: C, 53.91; H, 5.88; N, 18.80%; calculated for $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_3$: C, 53.81; H, 5.83; N, 18.83%. Thus, this azo compound was obtained in 85% yield.

(b) Reaction of Ic and lithium 2-nitropropan-2-ide in equimolar ratio in nitrogen atmosphere under ordinary laboratory lights, in the presence of cuprous bromide

A slurry of p-methoxybenzenediazonium fluoroborate (1.11 g; 5×10^{-3} mol) in 30 ml of methanol was reacted with lithium 2-nitropropan-2-ide (0.475 g; 5×10^{-3} mol) and cuprous bromide (0.072 g; 5×10^{-4} mol) taken in 30 ml of methanol, under nitrogen atmosphere. Rest of the reaction conditions were kept the same as in the reaction 7(a). The reaction commenced with evolution of nitrogen gas, and turned yellow in color. Nitrogen gas corresponding to 26% completion of the reaction was evolved in 15 min. Thereafter, no more nitrogen gas was evolved till 30 min. The reaction mixture was worked up as usual. The mixture of crude products was analyzed by GLC using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length. The products were identified by GLC analysis and their yields determined by the calibration method. The yields of various products identified were: anisole(20%), 2-(p-anisyl)-2-nitropropane(5%) and traces of

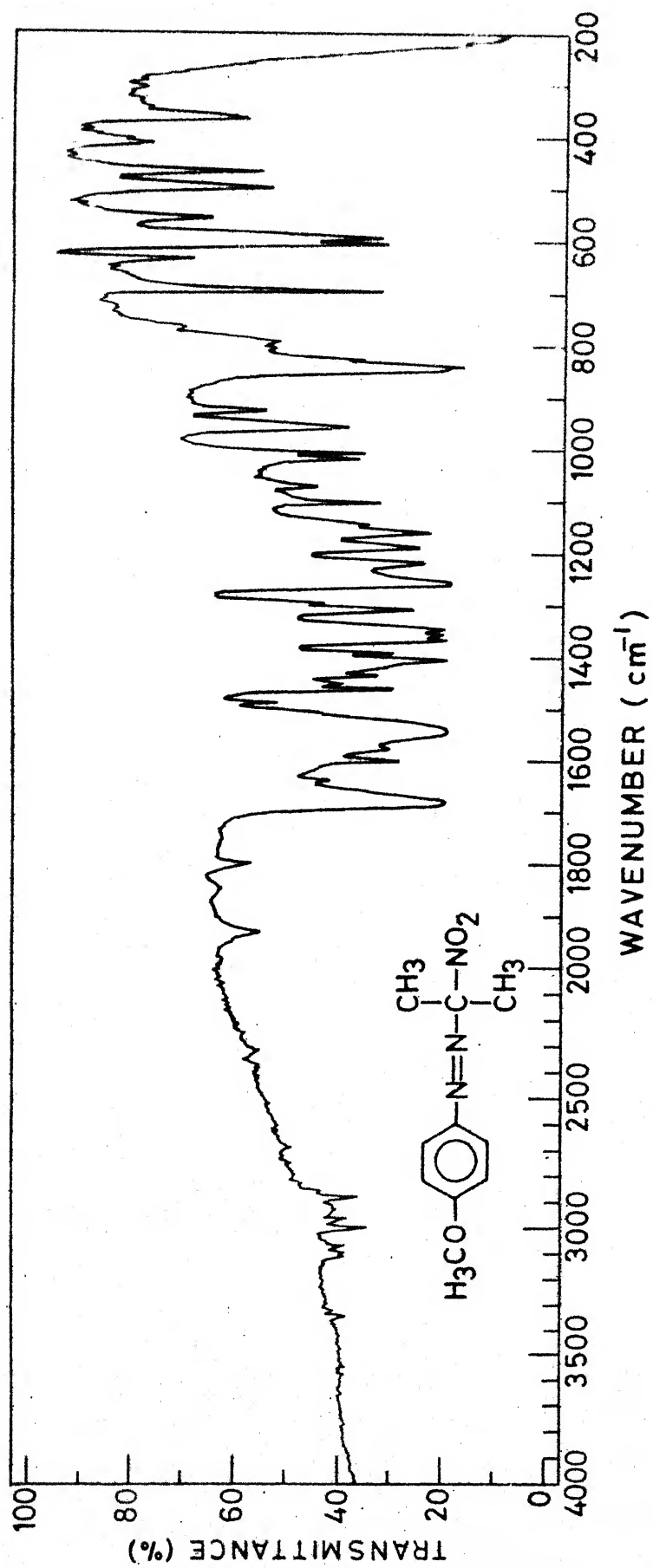


Fig. III.3 IR spectrum (KBr) of p-methoxybenzeneazo-2-(2-nitro)propane.

dimethoxybiphenyls. The product mixture was charged over a column of silica gel (100-200 M). Elution of the column with petroleum ether (b.p. 60-80°C) and benzene in the ratio 1:1, yielded p-methoxybenzeneazo-2-(2-nitro)propane (0.569 g; 51%). This compound was identified by its IR spectrum and elemental analysis. Formaldehyde, characterized and estimated as its dimedone derivative was obtained in 17% yield.

8. Stability of p-nitrobenzeneazo-2-(2-nitro)propane at 0°C

In a 3-neck RB flask, a solution of p-nitrobenzeneazo-2-(2-nitro)propane (1.19 g; 5×10^{-3} mol) in 30 ml methanol was placed. Nitrogen gas was bubbled through the solution for 30 min and the temperature maintained at 0°C. This solution was stirred for 180 min and no nitrogen gas was evolved, during this period. The reaction mixture was worked up as usual and chromatographed over a silica-gel (100-200 M) column. Elution with a mixture of petroleum ether (b.p. 60-80°C) and benzene in the ratio 3:1 yielded the starting p-nitrobenzeneazo-2-(2-nitro)propane (1.188 g; ca.100%). This was characterized by its IR spectrum and elemental analysis.

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CHAPTER IV

ELECTRON TRANSFER FREE RADICAL MECHANISM IN THE REACTIONS OF ARENEDIAZONIUM CATIONS WITH GRIGNARD REAGENTS

IV.1 Abstract

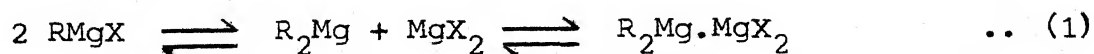
The reactions of arenediazonium fluoroborates, $p\text{-R-C}_6\text{H}_4\text{-N}_2^+\text{BF}_4^-$ (where $\text{R} = \text{H, OMe, NO}_2, \text{COCH}_3, \text{Me}$) with benzylmagnesium chloride and with tert.butylmagnesium chloride, $\text{R}'\text{-MgCl}$ in equimolar amounts, in THF at 30°C under nitrogen atmosphere have been found to yield, $\text{R-C}_6\text{H}_5$, $p\text{-R-C}_6\text{H}_4\text{-R}'$, $\text{R}'\text{-R}'$, $\text{R}'\text{-H}$ and mixtures of isomeric biaryls (excepting with $\text{R} = \text{H}$, when biphenyl was formed). Nitrogen contained in the arenediazonium salts was liberated to the extent of 80-90% in each of these reactions. The reactions were found to be inhibited in

the presence of α -methylstyrene. It has been proposed that the major pathway in these reactions involves an electron transfer from the Grignard reagent $R'-MgCl$ to the π -system of the arenediazonium cation, in a π -complex initially formed between the two reactants. Aryl and alkyl radicals produced, following the electron transfer, act as precursors of the products. Radicals have been detected by us in one of the reactions by the ESR method. It is found that only a minor component of the mechanism may involve the formation of azo compounds by an ionic pathway.

IV.2 Introduction

The discovery of Grignard reagents, reported in 1900 by Victor Grignard,¹ turned out to be the renaissance of synthetic organic chemistry. In spite of its tremendous synthetic utility, our understanding of the nature and structure of this reagent in solution and mechanism of its reactions has progressed at a very slow rate. The molecular structure of this reagent is seldom as simple as indicated by the popular formula $RMgX$.²

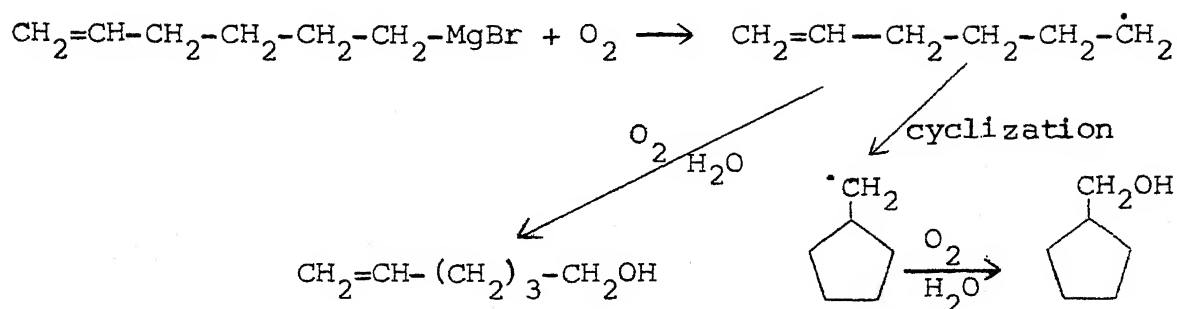
Schlenk and Schlenk³ proposed in 1929, that in solution, $RMgX$ is in equilibrium with R_2Mg (Eqn. 1):



Solids crystallized from Grignard solutions in ether have been demonstrated by Rundle and coworkers,⁴ with the help of X-ray

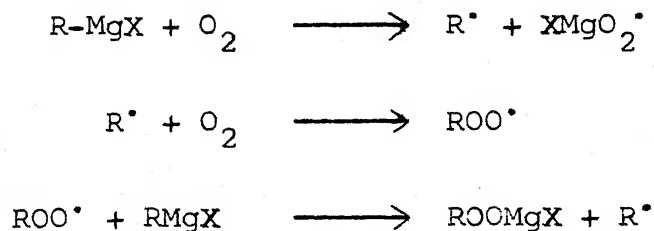
shown in Scheme IV.1:

SCHEME IV.1



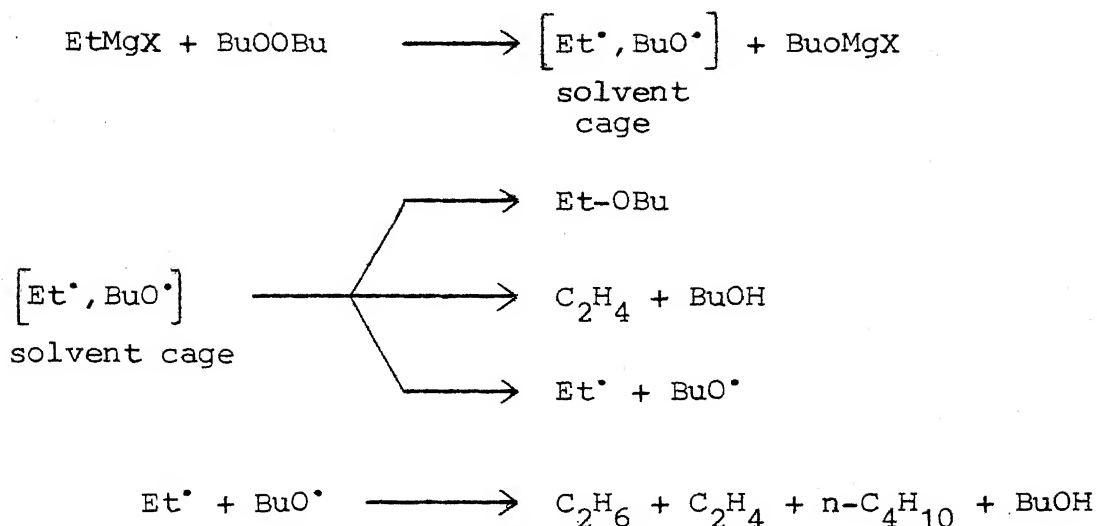
A single electron transfer free radical mechanism has been proposed for these autoxidation reactions (Scheme IV.2):

SCHEME IV.2



A similar mechanism has been reported for the autoxidation of hex-3,5-dienylmagnesium bromide.^{14a}

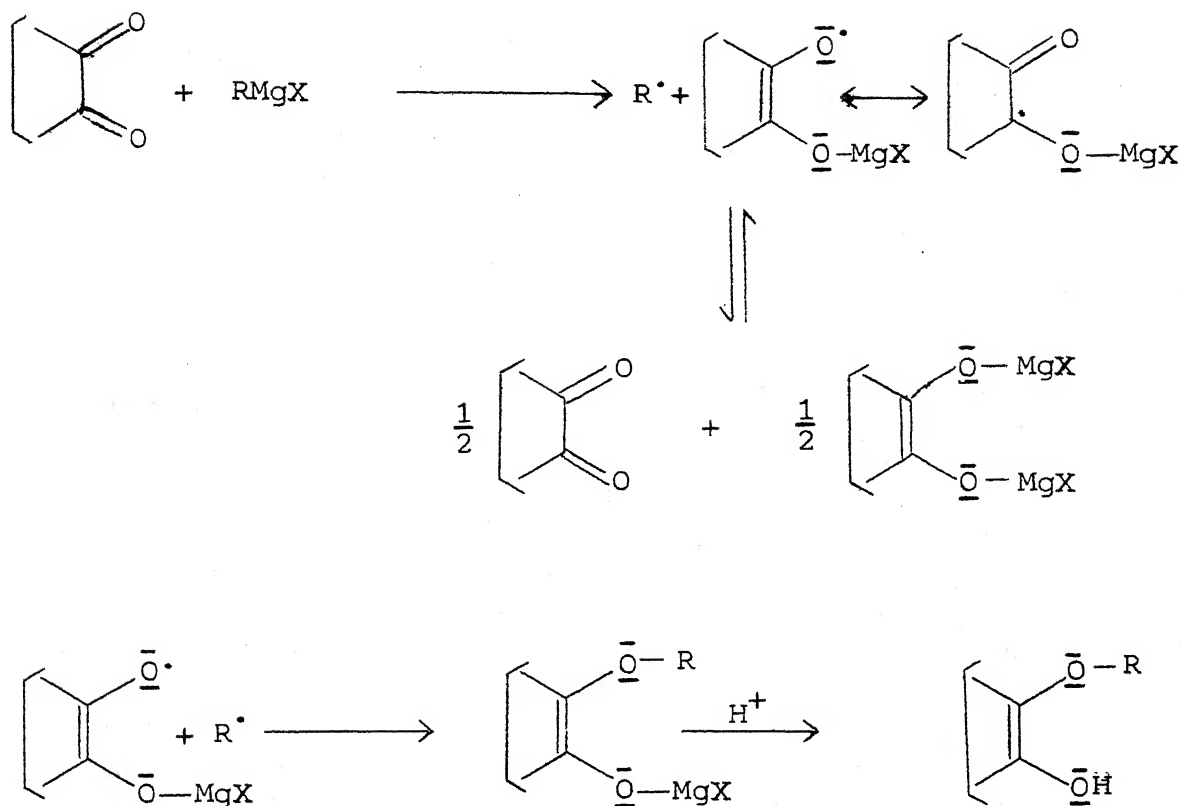
The reaction of Grignard reagents with peroxides which constitutes the second step of the overall net reaction with oxygen (Eqn. 3) has also been visualized^{14a, 26} as proceeding through a radical process. Kochi and coworkers²⁵ have proposed an electron transfer mechanism (Scheme IV.3) for such reactions on the basis of chemical and CIDNP studies:

SCHEME IV.3

The mechanism of the reaction of Grignard reagents with ketones is not well understood. These reactions are generally believed to proceed via an ionic mechanism. Reaction of benzophenone with Grignard reagent has received considerable attention.²⁷ In recent years, it has been conclusively proved with the help of chemical and ESR studies that in the reactions of Grignard reagents with certain carbonyl compounds, radicals are indeed the immediate precursors of the products.^{28,29}

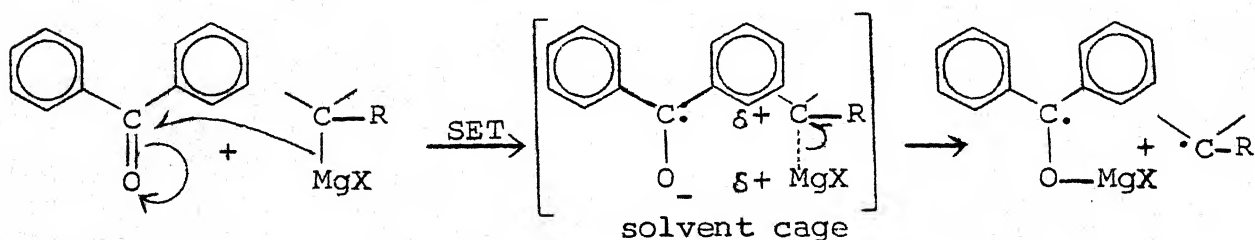
Blomberg and coworkers^{28f} have elucidated the mechanism of the reactions of Grignard reagents with orthoquinones, by using ESR technique. They found that these reactions involve free radical intermediates and proceed by the mechanism outlined in Scheme IV.4:

SCHEME IV.4



It has been suggested³⁰ that the polar and homolytic processes compete with each other, and by suitably manipulating the reaction conditions, one can make these reactions go exclusively along any one of the above mentioned pathways. A four-centre single electron transfer (SET) followed by homolysis, has been proposed^{16b} in the reactions of benzophenone with Grignard reagents (Scheme IV.5):

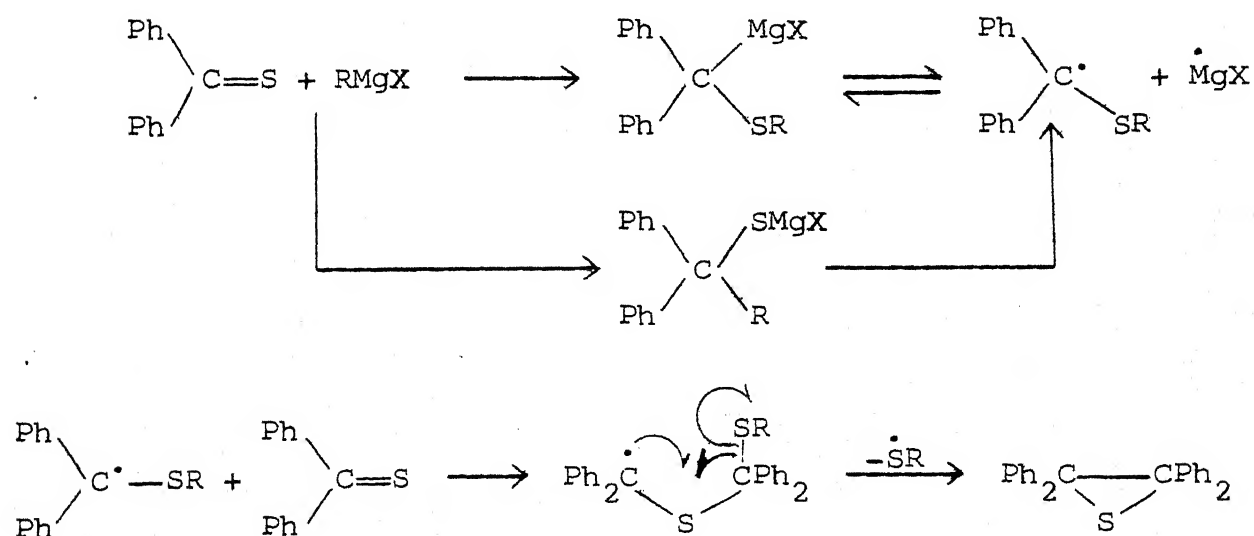
SCHEME IV.5



Recently, Ashby and coworkers³¹ have conclusively proved with the help of ESR evidence that an electron transfer mechanism is operative in the reactions of aromatic ketones with Grignard reagents.

The reactions of Grignard reagents with thiobenzophenone have been shown,³² with the help of ESR evidence, to follow a radical mechanism (Scheme IV.6):

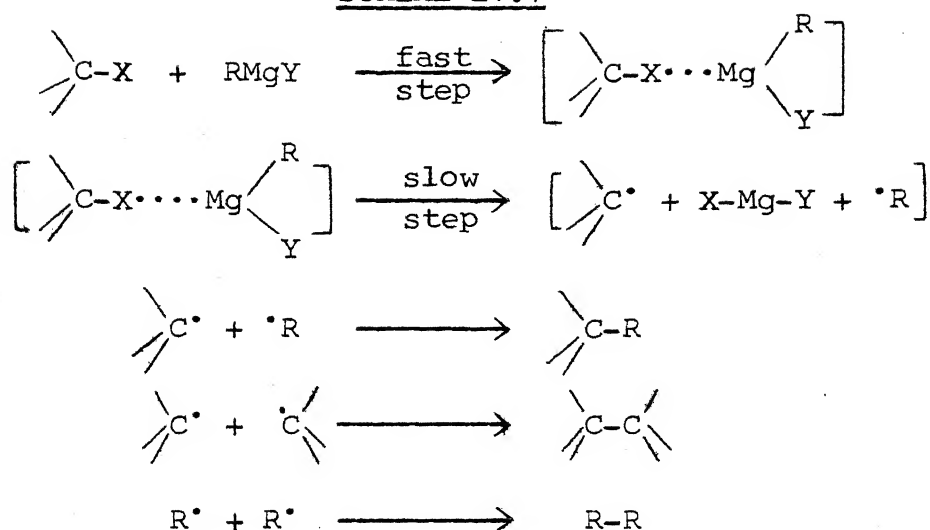
SCHEME IV.6



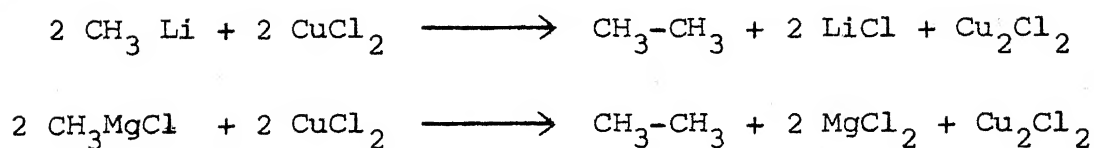
Singh and coworkers³³ have proposed electron transfer as the first step in the reactions of Grignard reagents with alkyl halides according to Scheme IV.7.

The oxidation of organomagnesium compounds and organolithium compounds has been accomplished using compounds of Cu(II) ^{34, 35} as outlined in Scheme IV.8.

SCHEME IV.7

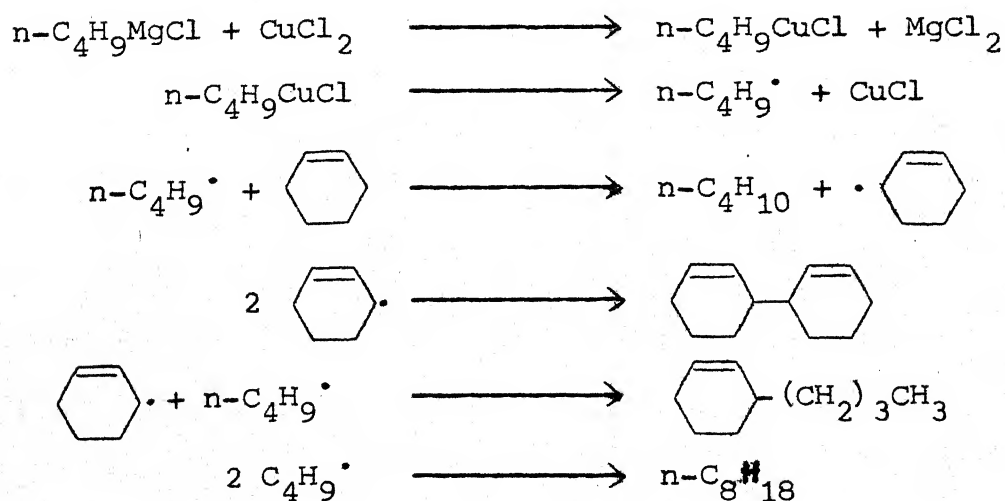


SCHEME IV.8



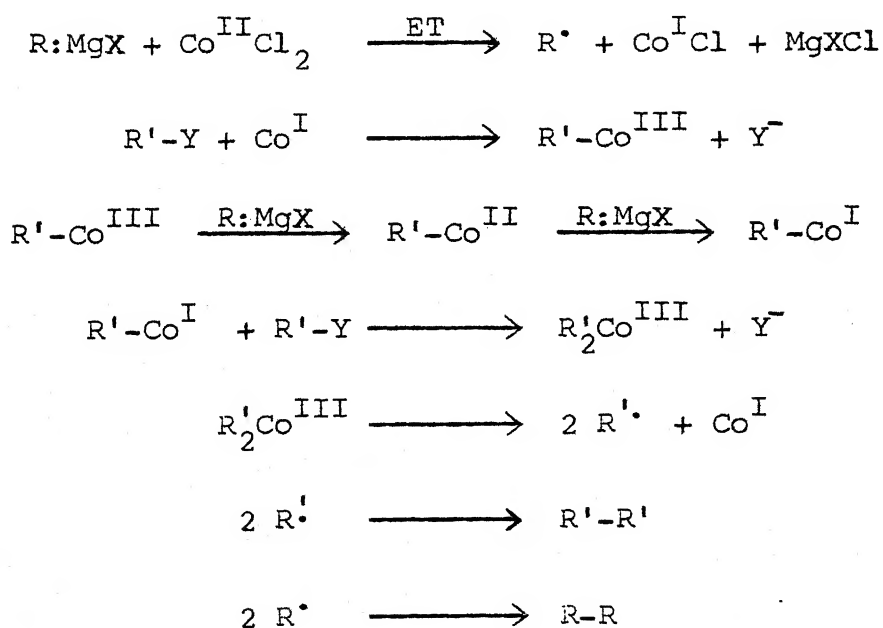
In the reaction of n-butylmagnesium chloride with cupric chloride, n-butyl radicals have been trapped by using cyclohexene.³⁶ 3,3'-Bicyclohexenyl has been isolated as one of the products in this reaction (Scheme IV.9):

SCHEME IV.9



Recently, Singh and coworkers³⁷ have found that the catalytic effect of cobalt compounds in the reactions of organic halides with Grignard reagents, resulting in enhanced yields of the homo-coupling products at the expense of the cross coupling products, may involve the 'super nucleophile' Co(I) as the active species. A chain mechanism has been proposed for these reactions (Scheme IV.10):

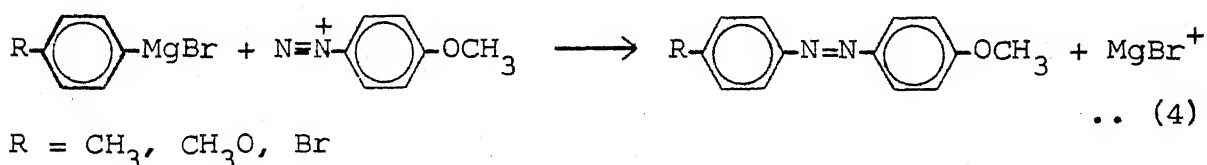
SCHEME IV.10



It is obvious from the above discussion that Grignard reagents are capable of reacting with appropriate substances as one-electron reductants.

The reactions of arenediazonium salts with Grignard reagents were first investigated by Hodgson and Marsden,³⁸ when they reported the formation of azo compounds in low yields.

On the other hand, Oda and coworkers^{39,40} have reported that the reactions of zinc chloride double salt of benzenediazonium chloride with alkyl- or arylmagnesium bromides give alkyl- or arylbenzenes in 6-34% yield. On re-investigation of some of these reactions, Curtin and Ursprung⁴¹ and Nomura⁴² confirmed the formation of azo compounds, but failed to obtain any significant amounts of biaryls. Nomura⁴³⁻⁴⁵ has utilized this reaction for the synthesis of a number of azo compounds which are formed in low yields. For example, substituted arylmagnesium bromides react with p-methoxybenzenediazonium cation, resulting in the formation of methoxyazobenzene derivatives in 0.9-30% yields⁴⁴ (Eqn. 4):



Treatment of methylmagnesium iodide with benzenediazonium fluoroborate has also been reported to give iodobenzene as a product.⁴¹

In view of the foregoing discussion and the known role of arenediazonium cations as good one electron oxidants (Section III.2), it was thought of interest to investigate the possible occurrence of an electron transfer free radical mechanism in the reactions of a few arenediazonium fluoroborates with Grignard reagents. Our investigations have revealed that the major reaction pathway does involve a single electron transfer from the

Grignard reagent to the arenediazonium cation, subsequently producing radicals, which serve as the immediate precursors of the final products.

IV.3 Results and Discussion

Reactions of arenediazonium cations with certain nucleophiles, earlier believed to occur by ionic mechanisms are now known⁴⁶⁻⁴⁸ to proceed via electron transfer free radical pathways. The reactions of arenediazonium cations with Grignard reagents are reported to give azo compounds in low yields.⁴³⁻⁴⁵ The reactions of zinc chloride double salt of benzenediazonium chloride with alkyl- or arylmagnesium bromides are known^{39,40} to give alkyl- or arylbenzenes in 6-34% yields. The mechanistic details of these reactions of arenediazonium cations with organometallics are obscure.^{10a}

In view of the immense synthetic utility of Grignard reagents as well as arenediazonium salts, the present study was undertaken to gain an insight into the mechanistic pathways operative in the reactions of certain arenediazonium cations with Grignard reagents. The reactions of five arenediazonium fluoroborates, $p\text{-R-C}_6\text{H}_4\text{-N}_2^+\text{BF}_4^-$ I, namely benzenediazonium fluoroborate, p-methoxybenzenediazonium fluoroborate, p-nitrobenzenediazonium fluoroborate, p-methylbenzenediazonium fluoroborate, and p-acetylbenzenediazonium fluoroborate with benzylmagnesium chloride IIa, and tert.butylmagnesium chloride IIb,

were examined under carefully varied conditions, in THF solvent under nitrogen atmosphere at 30°C. On addition of a solution of Grignard reagent in THF solvent to a slurry of arenediazonium salt, the reaction commenced immediately with vigorous evolution of nitrogen gas and the mixture turned homogeneous. The products obtained in the reactions of arenediazonium salts with benzylmagnesium chloride are summarized in Table IV.1 and those obtained in the reactions with tert.butylmagnesium chloride are listed in Table IV.2. A significant feature of these reactions is that in comparison to the reference substituent H in arenediazonium cations, p-NO₂ group accelerates while p-CH₃O group retards the reaction. This observation disfavors the existence of otherwise conceivable aryl cation intermediates in these reactions, since the formation of such intermediates would be retarded both in the case of p-methoxybenzenediazonium fluoroborate as well as p-nitrobenzenediazonium fluoroborate.⁴⁹ The formation of protodediazoniated products, R-C₆H₅ in high yields in these reactions, eliminates the possibility of bimolecular displacement of nitrogen as the reaction pathway. Furthermore, these reactions were found to be inhibited in the presence of α-methylstyrene. These facts strongly suggest the intervention of free radicals in the reactions under study. Indeed, strong ESR signals have been observed by us in the reaction of p-nitrobenzenediazonium fluoroborate with benzylmagnesium chloride, confirming the existence of radicals in this reaction. The ESR signals were absent in the pure reactants and were

TABLE IV.1: Reactions^a of Arenediazonium Fluoroborates
 $p\text{-R-C}_6\text{H}_4\text{-N}_2^+\text{BF}_4^-$, I with benzylmagnesium chloride IIa

Run	R	Rxn. Time (sec)	% Yield of Products ^b					
			Nitrogen	R-C ₆ H ₅	p-R-C ₆ H ₄ -CH ₂ -C ₆ H ₅	p-R-C ₆ H ₄ -C ₆ H ₄ -R (Isomeric mixture)	C ₆ H ₅ CH ₂ -CH ₂ C ₆ H ₅ ^c	C ₆ H ₅ CH ₃ ^c
1	H	50	85	60	9	4	30	24
2	OMe	60	80	57	13	3	27	22
3	OMe	1800	80	59	12	3	28	23
4	NO ₂	35	90	65	12	3	30	27
5	NO ₂	1800	90	67	12	3	32	28
6	COMe	45	90	66	14	2	31	28

a, Equimolar quantities of arenediazonium fluoroborate and benzylmagnesium chloride were reacted in THF medium at 30°C, under nitrogen atmosphere. Reaction mixtures were worked up soon after the nitrogen evolution stopped excepting in runs 3 and 5, where work up time was extended to 30 min.

b, Percentages based on arenediazonium fluoroborates unless otherwise specified. In addition, benzaldehyde phenylhydrazone (ca. 8%) in run 1 and N-benzyl benzaldehyde p-methoxyphenylhydrazone, IV (ca. 12%) each in runs 2 and 3 were also obtained. Additional colored mixture of products could not be analyzed.

c, Percentages based on benzylmagnesium chloride. Yields have been corrected after taking into account the amounts of these products formed during the preparation of benzylmagnesium chloride.

TABLE IV.2: Reactions^a of Arenediazonium Fluoroborates
 $p\text{-R-C}_6\text{H}_4\text{-N}_2^+\text{BF}_4^-$, I with tert. Butylmagnesium Chloride IIb

Run	R	Rxn. Time (sec)	% Yield of Products ^b					
			Nitrogen	$\text{R-C}_6\text{H}_5$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{p-R-C}_6\text{H}_4\text{-C-CH}_3 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{p-R-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-R} \\ \text{(Isomeric mixture)} \end{array}$	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{H}_3\text{C-C-C-CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$ c, d	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C-C-H} \\ \\ \text{CH}_3 \end{array}$ c, e
1	H	120	85	70	5	3	13	50
2	H	1800	85	71	5	3	14	50
3 ^f	H	2400	20	10	-	-	-	6
4	OMe	180	80	66	8	4	11	48
5	OMe	1800	80	65	8	4	12	50
6 ^f	OMe	2400	10	6	-	-	-	4
7	NO ₂	90	90	74	7	4	14	50
8 ^f	NO ₂	2400	25	15	-	-	-	10

a, Equimolar quantities of arenediazonium fluoroborate and tert. butylmagnesium chloride were reacted in THF medium at 30°C, under nitrogen atmosphere. Reaction mixtures were worked up soon after the nitrogen evolution stopped, excepting in runs 2 and 5, where work up time was extended to 30 min.

b, Percentages based on arenediazonium fluoroborates unless otherwise specified. In addition, benzeneazo- α,α -dimethylethane (ca. 7%) each in runs 1 and 2, besides a trace amount in run 3 and p-methoxybenzeneazo- α,α -dimethylethane (ca. 10%) each in runs 4 and 5, besides a trace amount in run 6, were also obtained. Additional colored mixture of products could not be analyzed.

c, Percentages based on tert. butylmagnesium chloride.

d, Yields have been corrected after taking into account the amounts of this product (GLC analysis) formed during the preparation of tert. butylmagnesium chloride.

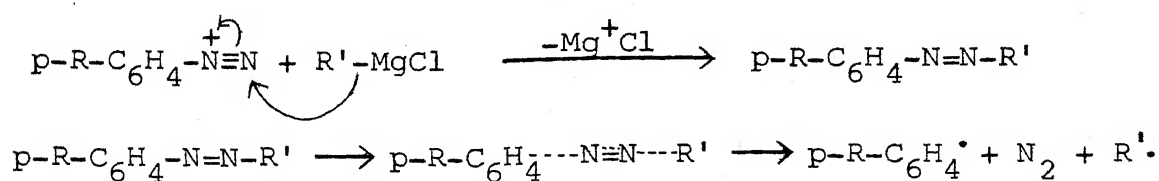
e, Mixture of nitrogen and methylpropane was analyzed by GLC.

f, In the presence of α -methylstyrene (0.1 mol).

observed only on mixing the two reagents.

It may be noticed that small amounts of azo compounds, namely benzeneazo- α,α -dimethylethane and p-methoxybenzeneazo- α,α -dimethylethane are formed in the reactions of benzenediazonium fluoroborate and p-methoxybenzenediazonium fluoroborate respectively, with tert.butylmagnesium chloride. Besides, small amounts of isomeric hydrazones, viz. benzaldehyde phenylhydrazone and N-benzyl benzaldehyde p-methoxyphenylhydrazone, in the reactions of benzenediazonium fluoroborate and p-methoxybenzenediazonium fluoroborate, respectively, with benzylmagnesium chloride, were also formed. Thus, an attractive possibility for the formation of radicals is the thermal homolytic cleavage of the two carbon-nitrogen bonds in the initially formed covalent azo compounds, as shown in Scheme IV.11:

SCHEME IV.11



The activation energies required for the dissociation of a few azo compounds, listed in Table IV.3, reflect that the rates of decomposition of these azo compounds are dependent on the stabilities of the incipient radicals formed in such decomposition reactions.⁵⁰

TABLE IV.3: Dissociation of azo Compounds ($R-N=N-R'$)

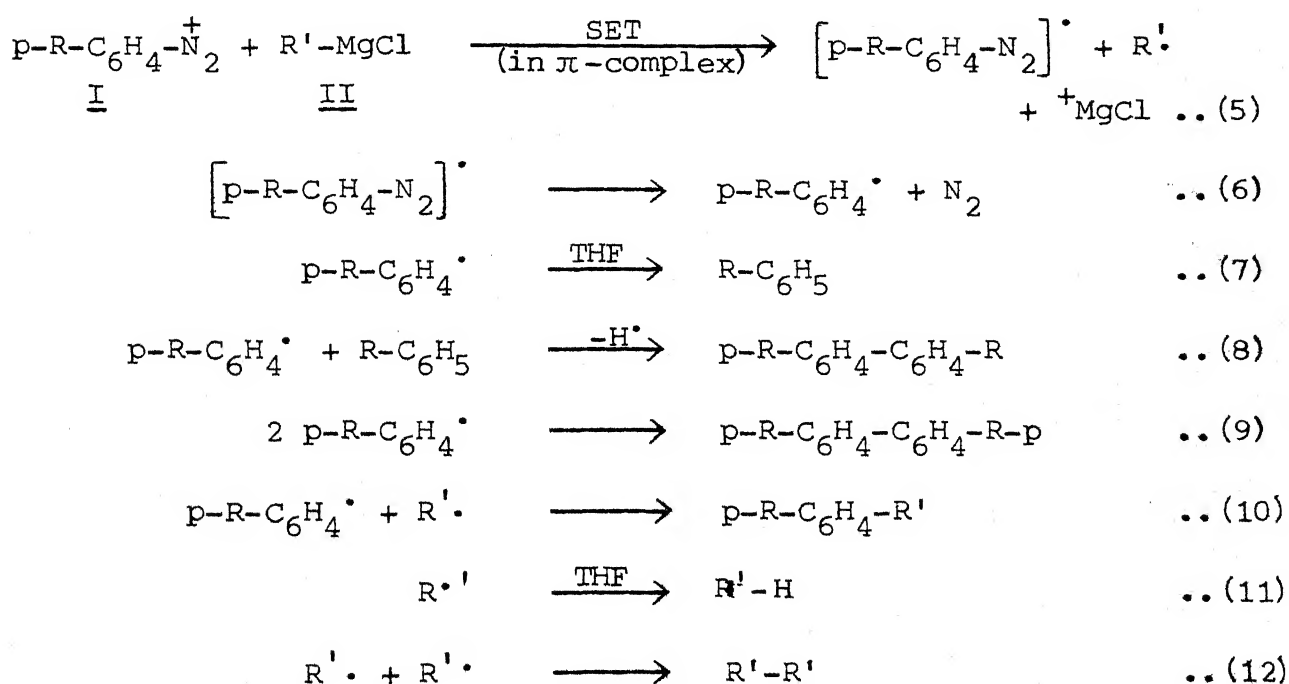
R	R'	Energy of activation (kcal/mol)	Solvent
CH_3	CH_3	51	Gas phase
<u>tert.</u> C_4H_9	<u>tert.</u> C_4H_9	43	Gas phase
Ph_2CH	Ph_2CH	27	Toluene
Ph	Ph_3C	27	Benzene
$\begin{array}{c} CN \\ \\ H_3C-C \\ \\ CH_3 \end{array}$	$\begin{array}{c} CN \\ \\ C-CH_3 \\ \\ CH_3 \end{array}$	31	Benzene

Thus, while azomethane $H_3C-N=N-CH_3$ undergoes thermal homolysis at significant rates only at temperatures near $400^\circ C$, the most common azo compound for the production of radicals,⁵⁰ namely azoisobutyronitrile $(CH_3)_2(CN)C-N=N-C(CN)(CH_3)_2$, has a half-life of 17 hr at $60^\circ C$. Similarly, diphenylmethylazodiphenylmethane,⁵¹ $Ph_2CH-N=N-CHPh_2$, phenylazotriphenylmethane,⁵² $Ph-N=N-CPh_3$ and phenylazophenylmethane⁵³ $Ph-N=N-CH_2Ph$, are also found to undergo thermal homolysis only above $45^\circ C$. All these compounds are stable at $30^\circ C$. Azo compounds likely to be encountered in our reactions, would be expected to be more stable than some of the azo compounds listed in Table IV.3, and thus their decomposition at our reaction temperatures ($30^\circ C$), would be highly unlikely. Indeed, it is observed that the product distribution obtained in our reactions remains essentially unaltered on extending the

reaction time. It is also known⁵⁰ that radicals do not induce decomposition of covalent azo compounds. These facts along with the observed low yields of azo compounds (or the isomeric hydrazones), where identified, among the products of our reactions, lead us to conclude that the formation of azo compounds by the expected ionic coupling does not constitute the major mechanistic pathway in these reactions. The path outlined in Scheme IV.11 is, therefore, completely ruled out. It is noteworthy in this context that while arenediazonium cations I act as good one electron oxidants in many reactions,⁴⁶⁻⁴⁸ Grignard reagents are capable of reacting with appropriate substrates as single electron reductants.^{31,33}

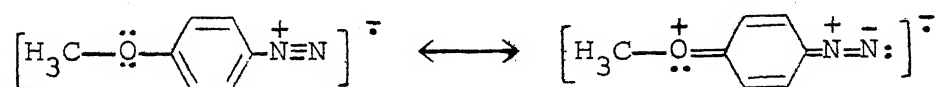
In view of the foregoing arguments, we propose a single electron transfer free radical mechanism outlined in Scheme IV.12 as the major pathway satisfactorily accounting for all the observations:

SCHEME IV.12



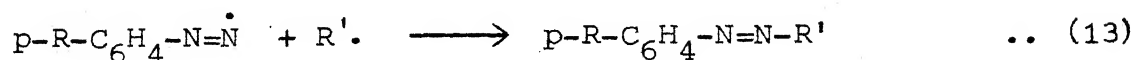
The reaction is initiated by a single electron transfer from the polar C-Mg bond of the Grignard reagent II to the arenediazonium cation I, via the formation of a π -complex.⁴⁸ The π interaction between the Grignard reagent and the arenediazonium cation, should be a facile process due to the delocalization of the positive charge over the aromatic ring of the arenediazonium cation. The resulting diazenyl radical $[p\text{-R-C}_6\text{H}_4\text{-N}_2]^{\cdot}$, may decompose by the heterolysis of the C-N bond,⁴⁶ yielding gaseous nitrogen and an electrophilic π -aryl radical. This π -aryl radical then reverts to a stable σ -aryl radical. The σ -aryl radical so formed then abstracts a hydrogen atom from the solvent (step 7), attacks the protodediazoniated products, $\text{R-C}_6\text{H}_5$ (step 8) or couples with another radical (step 9 and step 10). The aryl radicals being highly reactive and non-selective,⁵⁰ abstract hydrogen atoms from the solvent in preference over all other pathways consuming these. On the other hand, benzyl and tert.butyl radicals being more stable than the aryl radicals, dimerize to a larger extent, besides abstracting hydrogen atoms from the solvent. The observed difference in the reactivities of the two Grignard reagents may be related to the difference in stabilities of the alkyl radicals formed in step 5. Thus, benzylmagnesium chloride reacts faster than the tert.butylmagnesium chloride, owing to the higher stability of the resonance stabilized benzyl radical as compared to the tert.butyl radical. The reactivity sequence of the arenediazonium cations I, $p\text{-O}_2\text{N-C}_6\text{H}_4\text{-N}_2^+ > \text{C}_6\text{H}_5\text{-N}_2^+ > p\text{-MeO-C}_6\text{H}_4\text{-N}_2^+$, is in

agreement with their oxidation potentials.⁵⁴ Furthermore, the reaction with $p\text{-MeO-C}_6\text{H}_4\text{-N}_2^+$ is slowed down due to the slower heterolysis of the C-N bond in p-methoxyphenyldiazenyl radical, as this bond is strengthened^{46,55} due to direct conjugation between the -N_2^+ group and the -OCH_3 group in the diazenyl radical species as shown below:

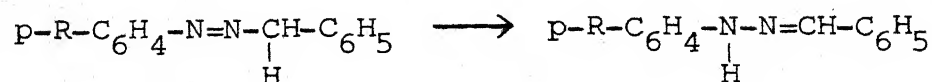


α -Methylstyrene inhibits the reaction presumably by scavenging the radicals⁵⁶ formed in steps 5 and 6.

Minor amounts of azo compounds formed, may either result by the coupling of the diazenyl radical with alkyl radical, before the former radicals undergo fragmentation⁵⁷ as shown in Eqn. 13 or by a minor ionic pathway outlined in the first step of Scheme IV.11.



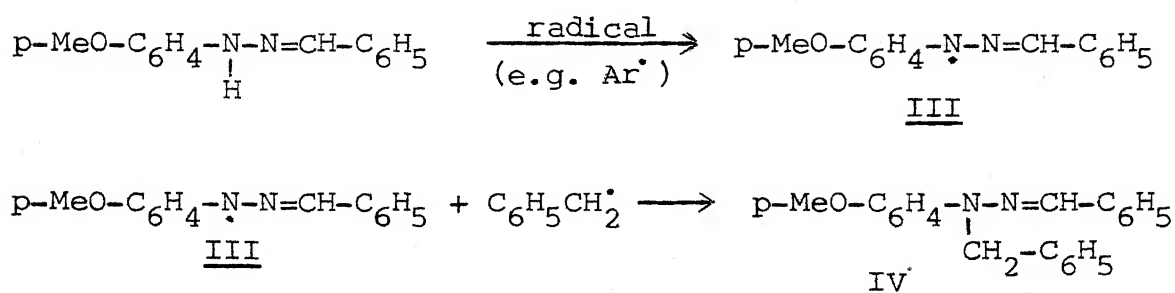
The azo compounds formed in the reactions with benzylmagnesium chloride isomerize to yield the corresponding substituted hydrazones:⁴¹



The N-benzyl benzaldehyde p-methoxyphenylhydrazone IV obtained

in runs 2 and 3 might arise by the coupling of a benzyl radical with radical III derived from the corresponding phenylhydrazone, by a hydrogen atom abstraction from the latter, as shown in Scheme IV.13:

SCHEME IV.13



Apparently, radical III is stabilized more by the presence of a p-MeO group in the phenyl ring, in contrast to other substituents and thus couples with a stable benzyl radical, to yield the product.

IV.4 Experimental

All melting points were determined on a MEL-TEMP melting point apparatus. IR spectra were recorded on Perkin-Elmer model-580 spectrophotometer. The GLC analyses were carried out on a chromatography and Instruments Company model AC1-FI instrument using 10% SE-30 on Crom-P (85-100 M) column of 2 m length. Column chromatography was carried out using activated silica-gel (100-200 M). Silica-gel (asc-India) was used for TLC analyses.

The ESR spectra were recorded on a Varian Model V-4502 EPR spectrophotometer operating at X-Band with 10 KC modulation. The NMR spectra were recorded on a Varian model A-60 spectrometer. Products of different reactions were identified by comparison of their IR spectra with those of the authentic samples, by TLC, GLC, mixed melting points and by C, H and N analyses. Literature melting points are cited from "Handbook of Chemistry and Physics," 50th edition, R.C. Weast (Ed.), published by Chemical Rubber Company, Cleveland, Ohio, unless otherwise stated.

Starting Materials

Tetrahydrofuran (THF) was purified by keeping it over potassium hydroxide pellets overnight, refluxing over sodium wire for 5-6 hr and then distilling over sodium twice, refluxing the same for 3-4 hr with lithium aluminium hydride (LAH) followed by a final distillation over LAH. The distilled THF was stored in contact with freshly drawn sodium wire.

Benzyl chloride (BDH) and tert.butyl chloride (SRL-India) were dried over anhydrous Na_2SO_4 and distilled before use. Magnesium metal (BDH, Poole, England, Grignard grade) was used after cleaning with methanol followed by ether and then drying in an oven at 60°C for 1 hr. Benzenediazonium fluoroborate, p-methoxybenzenediazonium fluoroborate, p-acetylbenzenediazonium fluoroborate, p-nitrobenzenediazonium fluoroborate and p-methylbenzenediazonium fluoroborate were prepared according to the procedure described in the literature.⁵⁸ The authentic samples of bibenzyl,⁵⁹

4-nitrodiphenylmethane,⁶⁰ 4-methoxydiphenylmethane,⁶¹ 4-acetyldiphenylmethane,⁶² 4-methyldiphenylmethane,⁶³ hexamethylethane,⁶⁴ tert.butylbenzene,⁶⁵ 4-methoxy-tert.butylbenzene,⁶⁶ 4-nitro-tert.butylbenzene,⁶⁷ 4,4'-dimethoxybiphenyl,⁶⁸ 4,4'-dinitrobiphenyl,⁶⁹ 4,4'-diacetylbiphenyl⁷⁰ and 4,4'-dimethylbiphenyl⁶⁸ were prepared by the methods reported in the literature. Authentic samples of biphenyl (BDH) and diphenylmethane were used after recrystallization. Authentic samples of benzaldehyde phenylhydrazone,⁶⁵ benzeneazo- α , α -dimethylethane,⁴¹ and p-methoxybenzeneazo- α , α -dimethylethane⁴¹ were also prepared by the known methods.

Preparation of Grignard reagents: Benzylmagnesium chloride and tert.butylmagnesium chloride

Benzylmagnesium chloride and tert.butylmagnesium chloride were prepared by standard procedures. In general, a perfectly clean and dry 3-neck 100 ml RB flask was mounted over a magnetic stirring base, fitted with a reflux condenser, a gas passing adaptor and a dropping funnel. Benzyl chloride (1.898 g; 0.015 mol) and tert.butyl chloride (1.388 g; 0.015 mol) were used for the preparation of the respective Grignard reagents. Clean and dry magnesium metal (0.365 g; 0.015 g-atom) was placed in the flask and covered with dry THF (10 ml). A small crystal of iodine was added and the reaction started by slow addition of the organic halide dissolved in dry THF (20 ml) over a period of 20 min with continuous bubbling of nitrogen gas through the reaction mixture. The reaction mixture was stirred for a period

of further 15 min and thereafter, refluxed till the entire quantity of magnesium dissolved (about 45 min). The reaction mixture was cooled and used for the reaction.

In an experiment designed to estimate⁷¹ the Grignard reagents, a 5 ml aliquot of the above Grignard reagent solution was added to 25 ml of 0.2 N hydrochloric acid and the excess of acid remaining unreacted back titrated with a standard NaOH solution (0.2 N), using phenolphthalein as indicator. Averages of closely agreeing runs and analyses showed that benzylmagnesium chloride was formed in 66.7% yield (ca. 0.01 mol) and tert.butylmagnesium chloride in 86.7% yield (ca. 0.013 mol). A separate experiment was conducted in each case, for the estimation of hydrocarbons and dimeric products formed during the preparation of Grignard reagent. On GLC analysis of benzylmagnesium chloride solution, toluene (18.3%) was found to have formed. On addition of the Grignard reagent into water, subsequent extraction with ether and GLC analysis of the ethereal extract, bibenzyl (15%) was found to have formed during the above preparation of benzylmagnesium chloride. Hexamethylethane (4.5%), along with an unestimated amount of methylpropane were formed during the preparation as described above, of tert.butylmagnesium chloride. These yields of the monomeric hydrocarbons and dimeric products were excluded from the yields of these products reported in the subsequent experiments of this section.

1. Reaction of benzenediazonium fluoroborate with an equimolar amount of benzylmagnesium chloride at room temperature (30°C) under nitrogen atmosphere. Reaction time - 50 sec (time for evolution of nitrogen gas)

A slurry of benzenediazonium fluoroborate (1.92 g; 0.01 mol) in 30 ml THF was taken in a 3-neck flask provided with a gas inlet tube, a pressure equalizing dropping funnel and connected to a gas collector through a mercury trap. The contents of the flask were flushed with pure dry nitrogen for 30 min under magnetic stirring. Benzylmagnesium chloride (0.01 mol) prepared as above, in 30 ml THF was added through the dropping funnel with continuous stirring. The reaction commenced immediately with evolution of nitrogen gas. The evolution of nitrogen gas ceased after 50 sec. and it was observed that 85% of the theoretical quantity of nitrogen gas had evolved during this period. The reddish brown reaction mixture was immediately poured into 100 ml of water acidified with 15 ml of hydrochloric acid, and extracted thrice with 100 ml portions of diethyl ether. The ethereal extract was washed well with water and dried over anhydrous MgSO_4 . Ether was removed carefully at room temperature under reduced pressure, till the volume of the ethereal extract was reduced to 50 ml. This crude mixture was analyzed by GLC, using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length. The products were identified by comparison of their retention times with those of the authentic samples. Product yields were estimated by comparison of the peak areas with those from equal aliquots of standard solutions of authentic samples

in ether. The yields of various products identified were estimated to be: benzene (60%), toluene (24%), biphenyl (4%), diphenylmethane (9%) and bibenzyl (30%). The yields of toluene and bibenzyl were corrected after taking into account the quantities of these materials formed during the preparation of benzylmagnesium chloride and were based on the latter. The reaction mixture was further concentrated and chromatographed over an activated silica-gel (100-200 M) column. Elution of the column with petroleum ether (b.p. 60-80°C) gave a mixture of biphenyl, bibenzyl and diphenylmethane. Further elution with a mixture of petroleum ether (b.p. 60-80°C) and benzene in the ratio 1:1 gave benzaldehyde phenylhydrazone (0.157 g; ca. 8%) m.p. 156°C; lit.⁶⁵ m.p. 158°C, identified by its superimposable IR spectrum with that of an authentic sample and mixed melting point technique.

2. Reactions of benzenediazonium fluoroborate with tert.butylmagnesium chloride at room temperature (30°C) under nitrogen atmosphere

(a) Reaction with equimolar amounts of benzenediazonium fluoroborate and tert.butylmagnesium chloride; Reaction time - 120 sec. (time for evolution of gas)

tert.Butylmagnesium chloride (0.013 mol) prepared from tert.butyl chloride (1.388 g; 0.015 mol) and magnesium (0.365 g; 0.015 g-atom) by the procedure mentioned earlier, was reacted with an equimolar amount of benzenediazonium fluoroborate (2.496 g; 0.013 mol) contained in THF (30 ml), in an assembly identical to that described for the reaction 1 above. The

reaction commenced immediately and a total of 393 ml (as at NTP) of the gas was evolved in 120 sec. GLC analysis of this gaseous mixture on a 10% SE-30 on Crom-P (85-100 M) column of 2 m length showed it to contain 50% methylpropane (yield based on tert.-butylmagnesium chloride). This product was identified by comparison of its retention time with that of an authentic sample, prepared by the addition of dil. HCl to tert.butylmagnesium chloride and collecting the gas evolved by the downward displacement of water. The yield was estimated by comparing the peak area with that from an equal aliquot of the authentic sample. Thus the rest of the gas, assumed to be nitrogen, corresponds to 85% of the theoretical quantity (yield based on benzenediazonium fluoroborate). After the evolution of the gas ceased, the reaction mixture was worked up immediately by adding it to 100 ml water acidified with 15 ml of hydrochloric acid. This solution was extracted with ether (3 x 100 ml) and the ethereal extract was washed with water, dried (anhydrous MgSO_4) and concentrated to a volume of 50 ml, by the removal of ether at room temperature under reduced pressure. This crude mixture of products was analyzed by GLC by the calibration method. The yields of the various products identified were: benzene (70%), hexamethylethane (13%), tert.butylbenzene (5%) and biphenyl (3%). The yield of hexamethylethane was based on tert.butylmagnesium chloride, while the yields of rest of the products were based on benzenediazonium fluoroborate. Also, the yield of hexamethylethane was corrected after taking into

account the amount of this material formed during the preparation of tert.butylmagnesium chloride. The solution of crude mixture of products in ether was further concentrated and chromatographed over a silica-gel (100-200 M) column. Elution with petroleum ether (b.p. 60-80°C) yielded a mixture of hydrocarbons. Further elution of the column with a mixture of petroleum ether (b.p. 60-80°C) and benzene in the ratio 3:1, yielded a yellow oil (0.147 g), which was identified by its superimposable IR spectrum with that of an authentic sample to be benzeneazo- α,α -dimethylethane. Its elemental analyses also agreed with the proposed structure. Thus the yield of this compound was 7%, based on benzenediazonium fluoroborate.

(b) Reaction of benzenediazonium fluoroborate with an equimolar amount of tert.butylmagnesium chloride; Reaction time - 1800 sec.

A slurry of benzenediazonium fluoroborate (2.496 g; 0.013 mol) in 30 ml THF was reacted with tert.butylmagnesium chloride (0.013 mol) in an identical manner as described in the previous experiment. Reaction commenced immediately with the evolution of gases (393 ml as at NTP) and was allowed to proceed for 30 min. GLC analysis of the gaseous mixture as described in the previous experiment showed it to contain 50% of methylpropane and 85% of nitrogen. Reaction mixture was worked up after 1800 sec with acidified water and extracted with ether. The ethereal extract, on GLC analyses, showed the product distribution

to be: benzene (71%), hexamethylethane (14%), tert.butylbenzene (5%) and biphenyl (3%). Column chromatography of the reaction mixture as described in the previous experiment yielded a mixture of hydrocarbons and benzeneazo- α,α -dimethylethane (0.147 g; ca. 7%).

(c) Reaction with equimolar amounts of benzenediazonium fluoroborate and tert.butylmagnesium chloride, in presence of α -methylstyrene. Reaction time - 2400 sec.

In a 3-neck RB flask mounted over a magnetic stirring base was placed benzenediazonium fluoroborate (2.496 g; 0.013 mol) and α -methylstyrene (11.82 g; 0.1 mol) contained in 30 ml THF. This mixture was flushed with dry nitrogen and tert.butylmagnesium chloride (0.013 mol) prepared in 30 ml THF added from a pressure equalizing dropping funnel. Reaction was allowed to proceed for 40 min. A gaseous mixture (76 ml as at NTP) was evolved. GLC analysis of this gaseous mixture in the usual manner gave methylpropane (6%). Thus, nitrogen in the gaseous mixture was 20%. On work up and product analyses in the manner described in the previous experiment, only benzene (10%) and a trace amount of benzeneazo- α,α -dimethylethane, could be detected besides an unestimated amount of α -methylstyrene. Small amounts of several other products, presumably formed by the trapping of radicals by α -methylstyrene, could not be analyzed.

3. Reactions of p-methoxybenzenediazonium fluoroborate with benzylmagnesium chloride at room temperature (30°C) under nitrogen atmosphere:

(a) Reaction with equimolar amounts of p-methoxybenzene-diazonium fluoroborate and benzylmagnesium chloride.

Reaction time - 60 sec. (time for the evolution of nitrogen gas)

A slurry of p-methoxybenzenediazonium fluoroborate (2.22 g; 0.01 mol) in 30 ml THF was reacted with benzylmagnesium chloride (0.01 mol) prepared in 30 ml THF, under conditions identical with those of the reaction (1). Nitrogen gas corresponding to 80% completion of the reaction was evolved in 60 sec, after which no more gas came out. The reaction mixture was worked up in the usual manner, by pouring it into acidified water. The ethereal extract of the reaction mixture was washed with water, dried (anhydrous MgSO_4), concentrated and analyzed by GLC on a 10% SE-30 on Crom-P (85-100 M) column of 2 m length. The distribution of products identified was: toluene (22%), anisole (57%), bibenzyl (27%), 4-methoxydiphenylmethane (13%) and a mixture of isomeric dimethoxybiphenyls (3%). The reaction mixture was concentrated further and chromatographed over a silica-gel (100-200 M) column. Elution with petroleum ether (b.p. 60-80°C) first gave bibenzyl (0.246 g; ca. 27%), m.p. 52°C, lit. m.p. 52.5°C; identified by mixed melting point and its superimposable IR spectrum with that of an authentic sample. Further elution of the column with a mixture of petroleum ether (b.p. 60-80°C) and benzene in the ratio 1:1, first gave a mixture of anisole and 4-methoxydiphenylmethane and thereafter, a pale yellow solid (0.38 g), which on recrystallization from ethanol gave a single spot on TLC, m.p. 123-124°C. The IR spectrum (Fig. IV.1) of this

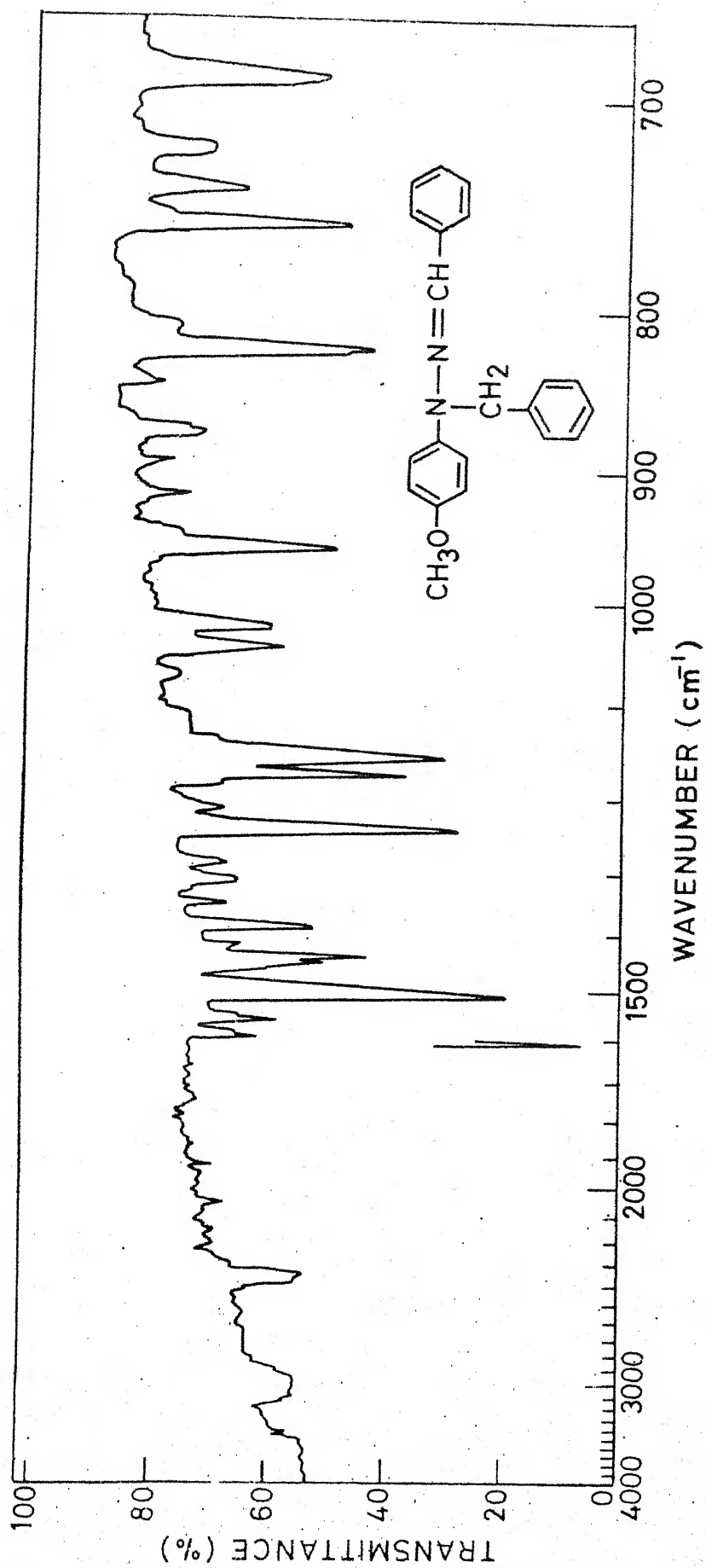


Fig. IV.1 IR spectrum (KBr) of Hydrazone IV .

compound recorded both in the form of KBr disc as well as in CCl_4 solution, did not indicate the presence of $-\text{NH}-$ group. It was identified to be $p\text{-H}_3\text{CO}-\text{C}_6\text{H}_4\text{-N}(\text{CH}_2\text{C}_6\text{H}_5)\text{-N}=\text{CH}-\text{C}_6\text{H}_5$ (obtained in 12% yield). Elemental analysis gave: C, 79.8; H, 6.45; N, 8.70%. $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}$ requires: C, 79.71; H, 6.37; N, 8.86%. The PMR spectrum, Fig. IV.2, of this compound showed distinct signals for the methoxy and methylene protons, but the signal for the methine proton appears to be buried under the signal for the aromatic protons. Further elution of the column with benzene yielded a pasty material which could not be analyzed.

(b) Reaction with equimolar amounts of p-methoxybenzenediazonium fluoroborate and benzylmagnesium chloride. Reaction time - 1800 sec

The reaction of p-methoxybenzenediazonium fluoroborate (2.22 g; 0.01 mol) in THF (30 ml) with benzylmagnesium chloride (0.01 mol) in 30 ml THF was performed under all conditions identical to those of the reaction 3(a), excepting that the reaction was allowed to proceed for 30 min. Nitrogen gas corresponding to 80% completion of the reaction was evolved in 60 sec. No further evolution of nitrogen took place. The reaction mixture was worked up in the usual manner and analyzed by GLC as described in the reaction 3(a). The yields of products identified were: toluene (23%), anisole (59%), bibenzyl (28%), 4-methoxydiphenylmethane (12%) and a mixture of isomeric biaryls (3%). Column chromatography of the reaction mixture as in the reaction 3(a) yielded bibenzyl (0.255 g ; ca. 28%), a mixture of

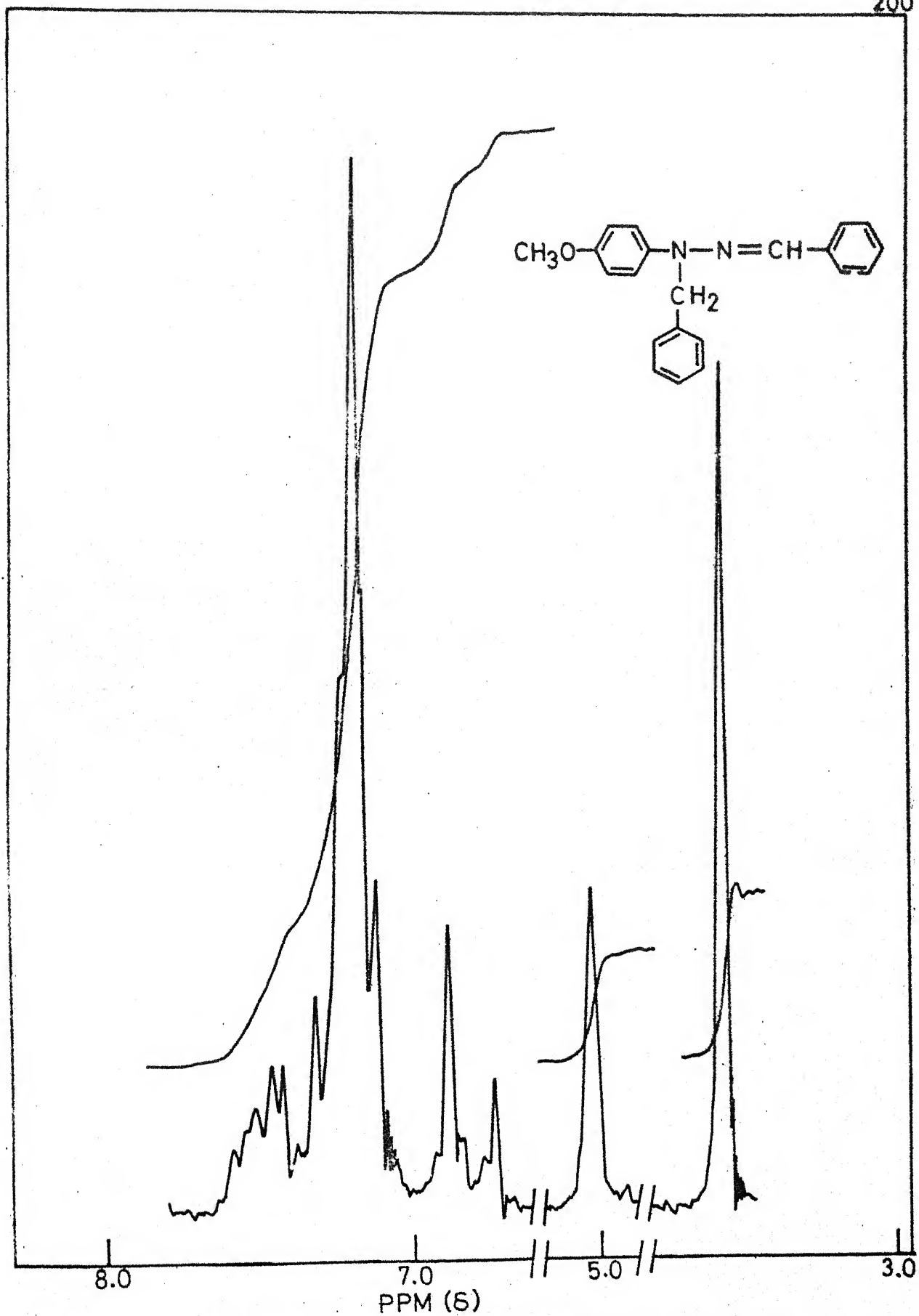


Fig.IV.2 NMR spectrum (60mcs) of Hydrazone IV.

anisole and 4-methoxydiphenylmethane, N-benzyl benzaldehyde p-methoxyphenylhydrazone (0.39g; ca. 12%) and a pasty material which could not be analyzed.

4. Reactions of p-methoxybenzenediazonium fluoroborate with tert.butylmagnesium chloride, at room temperature (30°C) under nitrogen atmosphere

- (a) Reaction with equimolar amounts of p-methoxybenzenediazonium fluoroborate and tert.butylmagnesium chloride. Reaction time - 180 sec. (time for the evolution of total amount of gaseous product)

A slurry of p-methoxybenzenediazonium fluoroborate (2.886 g; 0.013 mol) in 30 ml of THF was taken in a 3-neck flask, mounted over a magnetic stirring base, rest of the reaction conditions remaining the same as in the reaction 2(a). tert.-Butylmagnesium chloride (0.013 mol) contained in 30 ml THF was added from a pressure equalizing dropping funnel. The reaction commenced immediately and gaseous product (373 ml as at NTP) was evolved in 180 sec. GLC analysis of this gaseous product as described for the reaction 2(a), showed it to contain methylpropane (48%). Thus, the nitrogen evolved corresponded to 80% of the theoretical amount. The reaction mixture was worked up immediately after the evolution of gases stopped, by adding it to acidified water. The ethereal extract of the reaction mixture was washed with water, dried (anhydrous MgSO_4), concentrated and analyzed by GLC using the calibration method, as described for the reaction (1). The yields of various products

identified were: anisole (66%), hexamethylethane (11%), 4-methoxy-tert.butylbenzene (8%) and a mixture of isomeric dimethoxybiphenyls (4%). The reaction mixture was further concentrated and chromatographed over a silica-gel (100-200 M) column. Elution with petroleum ether (b.p. 60-80°C) yielded hexamethylethane (0.082 g; ca. 11%); m.p. 103°C; lit. m.p. 104°C, identified by its superimposable IR spectrum with that of the authentic sample and by mixed melting point technique. Further elution of the column with petroleum ether (b.p. 60-80°C) and benzene mixture in the ratio 1:1, yielded anisole (0.93 g; ca. 66%) followed by 4-methoxy-tert.butylbenzene (0.171; ca. 8%). These products were identified by their respective IR spectra which were superimposable with those of the authentic samples and elemental analyses. Further elution of the column with the same solvent gave an orange yellow oil identified as p-methoxy-azo- α,α -dimethylethane (0.25 g; ca. 10%). It was identified by its IR spectrum and elemental analysis. Anal.: C, 68.81; H, 8.42; N, 14.52%. Calculated for $C_{11}H_{16}N_2O$: C, 68.72; H, 8.39; N, 14.57%. Elution of the column with benzene gave a colored pasty material which could not be analyzed.

(h) Reaction with equimolar amounts of p-methoxybenzenediazonium fluoroborate and tert. butylmagnesium chloride. Reaction time - 1800 sec.

The reaction of p-methoxybenzenediazonium fluoroborate (2.886 g; 0.013 mol) in THF (30 ml) with tert.butylmagnesium

chloride (0.013 mol) in 30 ml of THF was performed under the conditions identical to those of the reaction 4(a), excepting that the reaction time was extended to 30 min. The mixture of gases obtained, on GLC analysis, yielded 50% methylpropane and the nitrogen was calculated to have evolved in 80% yield. The reaction mixture was worked up in the usual manner and analyzed by GLC and column chromatography as described in the reaction 4(a). The yields of various products identified were: anisole (65%), hexamethylethane (0.089 g; 12%), 4-methoxy-tert.butylbenzene (8%), mixture of isomeric dimethoxybiphenyls (4%) and p-methoxybenzeneazo- α,α -dimethylethane (0.25 g; 10%). All the compounds were characterized either by GLC or by a comparison of their IR spectra with those of the authentic samples and their elemental analyses. Additional colored pasty materials could not be analyzed.

(c) Reaction with equimolar amounts of p-methoxybenzenediazonium fluoroborate and tert.butylmagnesium chloride, in presence of α -methylstyrene. Reaction time - 2400 sec.

In a 3-neck RB flask, mounted over a magnetic stirring base was placed p-methoxybenzenediazonium fluoroborate (2.886 g; 0.013 mol) and α -methylstyrene (11.82 g; 0.1 mol) contained in 30 ml of THF. The system was flushed with dry nitrogen for 30 min and then tert.butylmagnesium chloride (0.013 mol) in 30 ml of THF was added to the flask from a pressure equalizing dropping funnel. Reaction was allowed to proceed for 40 min. The gaseous products evolved (41 ml as at NTP) on GLC analysis

as for the previous experiments, showed it to be a mixture of methylpropane and nitrogen in 4% and 10% yields of the theoretical, respectively. On work up and product analyses in the manner described for the reaction 4(a), only anisole (6%) and a trace amount of p-methoxybenzeneazo- α,α -dimethylethane could be detected, besides an unestimated amount of α -methylstyrene. Additional colored pasty material could not be analyzed.

5. Reactions of p-nitrobenzenediazonium fluoroborate with benzylmagnesium chloride at room temperature (30°C) under nitrogen atmosphere

- (a) Reaction with equimolar amounts of p-nitrobenzenediazonium fluoroborate and benzylmagnesium chloride. Reaction time - 35 sec. (time for the complete evolution of nitrogen gas)

A slurry of p-nitrobenzenediazonium fluoroborate (2.37 g; 0.01 mol) in 30 ml of THF was taken in a 3-neck RB flask, mounted over a magnetic stirring base and provided with a gas inlet tube, a condenser and a pressure equalizing dropping funnel. The gas outlet was connected to a collector through a mercury trap. The contents of the flask were flushed with dry nitrogen for 30 min. Benzylmagnesium chloride (0.01 mol) contained in 30 ml of THF was added through the dropping funnel with continuous stirring. The reaction commenced immediately with the evolution of nitrogen gas. Nitrogen gas corresponding to 90% completion of the reaction was evolved in 35 sec, after which no more gas evolved. The reddish brown reaction mixture

was added to acidified water and the mixture extracted with ether (3 x 100 ml). The ethereal extract was washed with water, dried (anhydrous MgSO_4) and concentrated to a volume of 50 ml. The mixture of products was analyzed by GLC using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length, by the calibration method. The yields of various products identified were: toluene (27%), nitrobenzene (65%), bibenzyl (30%), 4-nitrodiphenylmethane (12%) and a mixture of isomeric dinitrobiphenyls (3%). The reaction mixture was chromatographed over a silica-gel (100-200 M) column. Elution of the column with petroleum ether (b.p. 60-80°C) gave bibenzyl (0.273 g; ca. 30%); m.p. 52°C; lit. m.p. 52.5°C, identified by its superimposable IR spectrum with that of an authentic sample and mixed melting point technique. Elution of the column with petroleum ether (b.p. 60-80°C) and benzene mixture in 1:1 ratio (v/v), gave a liquid product. This was characterized as nitrobenzene (0.80 g; ca. 65%) by its superimposable IR spectrum with that of an authentic sample and by GLC. Further elution of the column with petroleum ether (b.p. 60-80°C) and benzene mixture in 1:1 ratio, gave a red colored mixture of products. These products could not be separated, but GLC analysis showed the presence of 4-nitrodiphenylmethane. Continued elution of the column with benzene first gave a yellow solid, the elemental analysis of which showed it to be a compound with empirical formula $\text{C}_6\text{H}_4\text{NO}_2$. Its spot of TLC and retention time on GLC matched with corresponding characteristics of 4,4'-dinitrobiphenyl, but its mixed melting point with an authentic sample of 4,4'-dinitrobiphenyl

was depressed, indicating it to be a mixture of isomeric dinitrobiphenyls (0.037g; ca. 3%). Further elution of the column with benzene gave a dark colored pasty material which could not be analyzed.

In a separate experiment, when the reactants were mixed in the cavity of ESR spectrophotometer, ESR signals, (Fig. IV.3) were observed. These signals were not observable with any of the pure reactants.

(b) Reaction with equimolar amounts of p-nitrobenzenediazonium fluoroborate and benzylmagnesium chloride. Reaction time - 1800 sec.

The reaction of p-nitrobenzenediazonium fluoroborate (2.37 g; 0.01 mol) in dry THF (30 ml) with benzylmagnesium chloride (0.01 mol) contained in 30 ml of THF was performed under conditions identical to those of the reaction 5(a), excepting that the reaction time was extended to 30 min. The nitrogen gas evolved corresponded to 90% completion of the reaction. The reaction mixture was worked up as usual and analyzed by GLC and column chromatography as described for the reaction 5(a). The yields of various products identified were: toluene (28%), nitrobenzene (0.824 g; ca. 67%), bibenzyl (0.291 g; 32%), 4-nitrodiphenylmethane (12%) and a mixture of isomeric dinitrobiphenyls (0.037 g; ca. 3%). Additional colored mixture of products could not be analyzed.

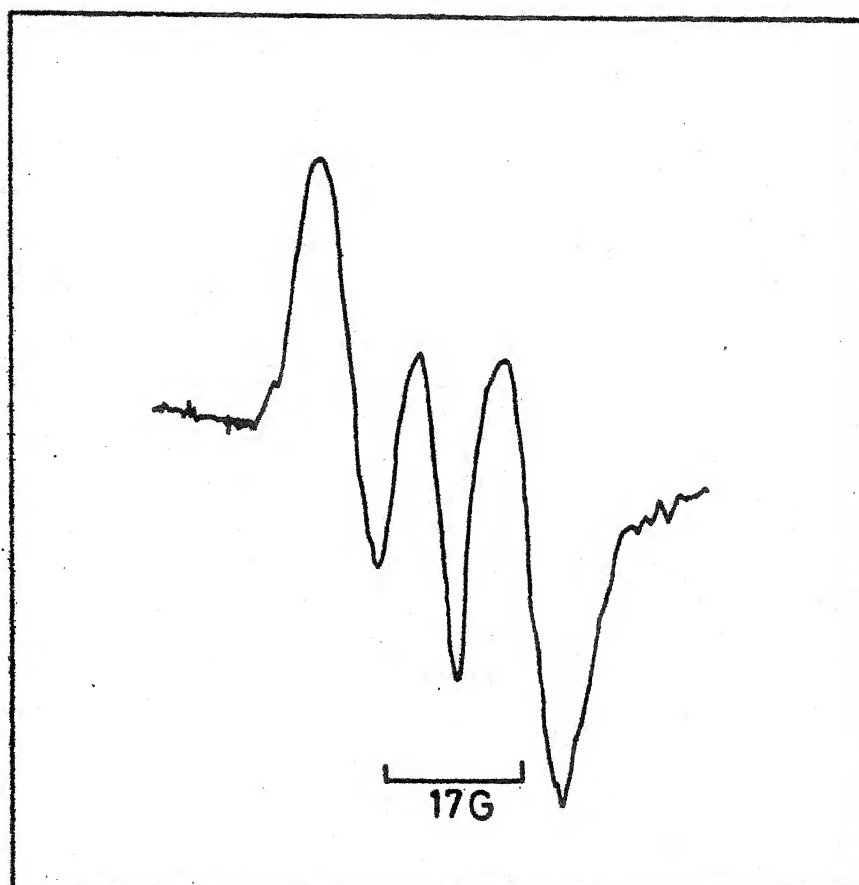


Fig.IV.3 ESR obtained during the reaction of p-nitrobenzene diazonium fluoroborate with benzylmagnesiumchloride .

6. Reactions of p-nitrobenzenediazonium fluoroborate with tert.butylmagnesium chloride under nitrogen atmosphere at room temperature (30°C)
- (a) Reaction with equimolar amounts of p-nitrobenzenediazonium fluoro-borate with tert.butylmagnesium chloride. Reaction time - 90 sec. (time for the total amount of gaseous product evolution)

A slurry of p-nitrobenzenediazonium fluoroborate (3.081 g; 0.013 mol) in 30 ml of dry THF was taken in a 3-neck RB flask, mounted over a magnetic stirring base and reacted with tert.butylmagnesium chloride (0.013 mol) contained in dry THF (30 ml), under nitrogen atmosphere and at room temperature (30°C). The reaction commenced immediately and a mixture of gases (408 ml as at NTP) were evolved in 90 sec. GLC analysis of this gaseous mixture using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length showed it to contain 50% of methylpropane (yield based on tert.butylmagnesium chloride). Thus, the rest of the gas, assumed to be nitrogen, is evolved in 90% of the theoretical yield. The reaction mixture was worked up immediately by adding it to acidified water and extracted with ether (3 x 100 ml). The ethereal extract was washed with water, dried (anhydrous MgSO_4), concentrated at room temperature under reduced pressure and analyzed by GLC, as described for the reaction 2(a). The yields of various products identified were: hexamethylethane (14%), nitrobenzene (74%), p-nitro-tert.butylbenzene (7%) and a mixture of isomeric dinitrobiphenyls (4%). The reaction mixture was chromatographed over a column of silica-gel (100-200 M).

on work up as usual and analysis by GLC as well as column chromatography as described in the reaction 6(a) above, yielded only nitrobenzene (15%), besides an unestimated amount of α -methylstyrene. Additional colored pasty material could not be analyzed.

7. Reaction of p-acetylbenzenediazonium fluoroborate with an equimolar amount of benzylmagnesium chloride at room temperature (30°C) under nitrogen atmosphere. Reaction time - 45 sec. (time for evolution of nitrogen gas)

The reaction of p-acetylbenzenediazonium fluoroborate (2.34 g; 0.01 mol) contained in THF (30 ml) with benzylmagnesium chloride (0.01 mol) contained in 30 ml of THF was performed under reaction conditions identical to those of the reaction (1). The reaction commenced with vigorous evolution of nitrogen gas, which amounted to 90% yield of the theoretical quantity, in 45 sec. The reaction mixture was worked up in the usual manner and the ethereal extract analyzed by GLC as described for the reaction (1). The yields of various products identified were: toluene (28%), acetophenone (66%), bibenzyl (31%), p-acetyldiphenylmethane (14%) and a mixture of isomeric diacetylbiphenyls (2%). The mixture of products was chromatographed over a silica gel (100-200 M) column. Elution with petroleum ether (b.p. 60-80°C) gave bibenzyl (0.282 g; ca. 31%); m.p. 52°C; lit. m.p. 52.5°C. Further elution of the column with petroleum ether (b.p. 60-80°C) and benzene mixture (1:1) gave a liquid which was analyzed by GLC and found to be a mixture of acetophenone (66%)

and p-acetyldiphenylmethane (14%). Further elution of the column with benzene yielded a colored pasty material, which could not be analyzed.

8. Reaction of p-methylbenzenediazonium fluoroborate with benzylmagnesium chloride at room temperature under nitrogen atmosphere

The reaction of p-methylbenzenediazonium fluoroborate (2.06 g; 0.01 mol) taken in THF (30 ml) with benzylmagnesium chloride (0.01 mol) contained in 30 ml of THF was carried out under reaction conditions identical to those of the reaction (1). Nitrogen gas corresponding to 85% completion of the reaction was evolved in 50 sec. The reaction mixture was worked up as usual and the ethereal extract washed with water, dried (anhydrous MgSO_4) and concentrated at room temperature under reduced pressure. GLC analysis of the reaction mixture by the calibration method yielded the product distribution: toluene (86%), bibenzyl (32%), p-methyldiphenylmethane (10%) and a mixture of isomeric dimethylbiphenyls (3%). It is evident from the product distribution obtained in the reaction (1) and the yields of toluene obtained in the reactions of arenediazonium salts with benzylmagnesium chloride, that a maximum of 25% of toluene is formed by the hydrogen atom abstraction by benzyl radicals and thus the rest 61% is obtained from the p-methylphenyl radicals. The reaction mixture obtained in the above reaction was concentrated further and chromatographed over a silica gel

(100-200 M) column. Elution with petroleum ether (b.p. 60-66°C) gave bibenzyl (0.291 g; ca. 32%); m.p. 52°C; lit. m.p. 52.5°C. Further elution of the column with petroleum ether (b.p. 60-80°C) yielded p-methyldiphenylmethane (0.182 g; ca. 10%); b.p. 144°C (16 mm); lit. b.p. 144°C (16 mm). Further elution of the column gave only colored tarry material which could not be analyzed.

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CHAPTER V

ELECTRON TRANSFER MECHANISMS IN THE REDUCTIVE DEMERCURATION AND SYMMETRI- ZATION OF ORGANOMERCURIC HALIDES WITH SODIUM NAPHTHALENE AND LITHIUM ALUMINIUM HYDRIDE

V.1 Abstract

The reactions of a few alkyl- and arylmercuric chlorides $R-Hg-Cl$ viz., benzylmercuric chloride, phenylmercuric chloride, p-tolylmercuric chloride and p-nitrophenylmercuric chloride with varying amounts of sodium naphthalene in THF solvent, at $30^{\circ}C$ under nitrogen atmosphere were examined. Each of these reactions commenced with immediate precipitation of metallic mercury. Besides, naphthalene, symmetrical diorganomercurials $R-Hg-R$, monomeric hydrocarbon $R-H$ and dimeric products $R-R$ were obtained

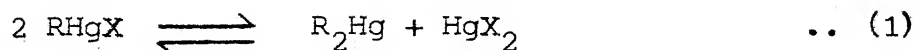
as other products. Though the reactions of organomercuric halides with equimolar quantities of sodium naphthalene were largely incomplete in 30 min., more of each halide was consumed on increasing the reaction time. The reactions were complete with twice the molar quantity of sodium naphthalene, excepting in case of p-tolylmercuric chloride, which reacted to an extent of 88% only. A novel electron transfer free radical mechanism involving the occurrence of a $\pi^* \rightarrow \pi^*$ electron transfer from the naphthalene radical anion to R-Hg-Cl, has been proposed to account for the observed facts. Most reasonable process leading to the radical induced symmetrization of R-Hg-Cl, in the presence of an electron donor, has been identified.

The reactions of the same four organomercuric chlorides as mentioned above, with LiAlH_4 in THF solvent at 30°C under dry nitrogen, commenced with the evolution of hydrogen gas and simultaneous separation of metallic mercury. Each organomercuric halide R-Hg-Cl, completely reacted with an equimolar amount of LiAlH_4 , yielding R-Hg-R, R-H and R-R. Symmetrization of arylmercuric halides in these reactions has been observed first time. Our observations rule out the possibility of formation of hypothetical R-Hg-H, in these reactions. A new electron transfer mechanism has been proposed which satisfactorily accounts for the initial generation of radical intermediate, besides rationalizing all the observations recorded for these reactions.

V.2 Introduction

Frankland's¹ initial studies on the preparation of organomercurials have been followed by an ever-increasing interest in the properties and reactions of these materials. An account of the early history and important developments in organomercury chemistry can be found in Whitmore's treatise.² A wide range of organometallic and organo-elemental compounds have been prepared from organomercury compounds by their reactions with halides of other metals and non-metals and also by the action of free metals, resulting in organometallic compounds of the latter (i.e. other metals actually used).³

Since most methods of synthesizing the organomercury compounds lead to derivatives RHgX , symmetrization (i.e. the conversion of RHgX salts into fully substituted diorganomercurials R_2Hg), is one of the most important reactions of organomercury derivatives. Schematically, the process may be visualized as an equilibrium between the organomercury salt and the symmetrization products (Eq. 1):

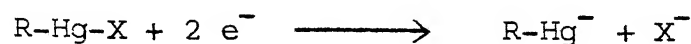
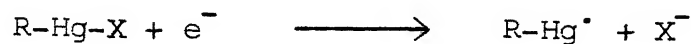


The equilibrium in most cases lies far to the left; hence the true equilibrium must be displaced to cause symmetrization. This is usually accomplished by either removing the mercuric halide reactant, often by complex formation,⁴ or by removing the mercuric ion as metallic mercury via reduction of RHgX . Though

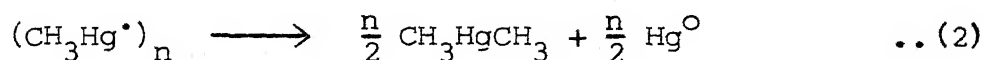
the product of reduction of an organomercurial is often the same as the product of symmetrization, in certain cases reductive demercuration also occurs.

Alkyl or arylmercuric salts may be reduced by one-electron or two-electron transfer processes, as shown in Scheme V.1. The source of electrons may be a cathode, a metal or another reducing agent e.g., sodium stannite or hydrazine:

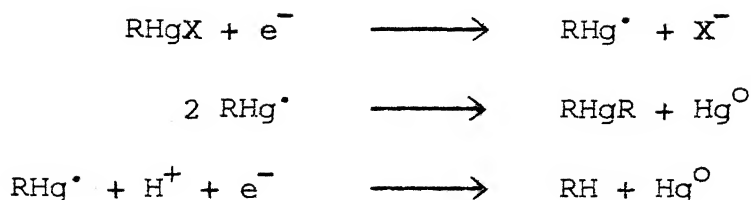
SCHEME V.1



Kraus⁵ demonstrated in 1913 that many alkylmercuric halides can be reduced electrolytically. Electrolysis of methylmercuric chloride in liquid ammonia, for instance, gives a dark spongy precipitate at the cathode. This precipitate is a good electrical conductor and has been described as $(\text{CH}_3\text{Hg}^\bullet)_n$. On warming, this material gives metallic mercury and dimethylmercury in an exothermic reaction (Eq. 2):

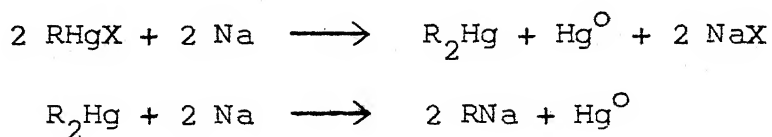


Polarographic studies carried out by Benesch and Benesch⁶ on a number of alkylmercuric salts, established that the reduction can either be a one electron or a two electron process depending upon the potential applied. The available evidence supports the mechanism shown in Scheme V.2:

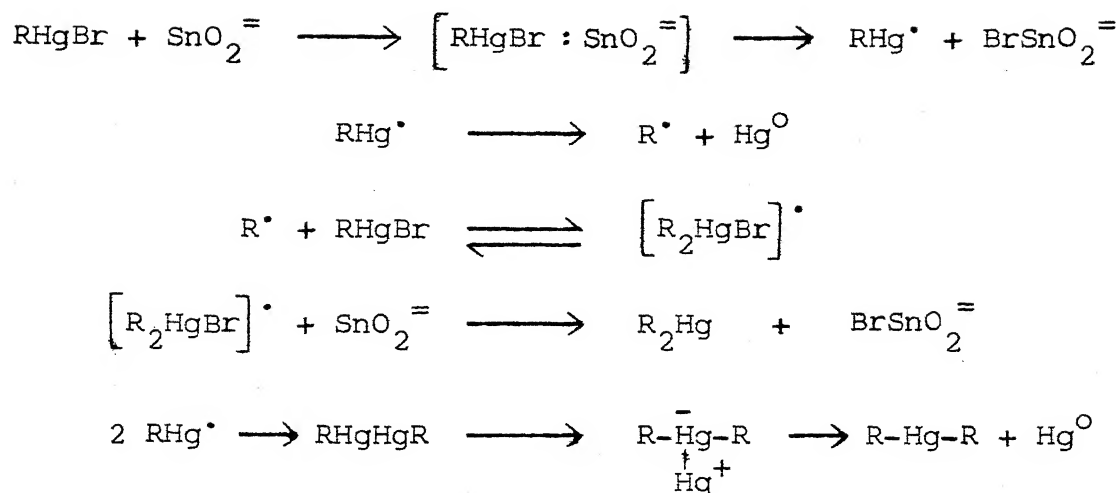
SCHEME V.2

The path taken by RHg^\bullet depends upon its concentration, the applied potential and the acid concentration.

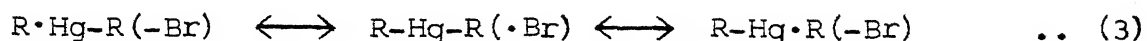
Electropositive metals react with organomercurials by an oxidation-reduction process. The reduction usually proceeds fast to give initially the diorganomercury compound and metallic mercury; and thereafter, more slowly to give the metal-alkyl and more free mercury. The electropositive metals which have been employed are sodium,^{7,8} copper,⁹⁻¹¹ zinc,¹² magnesium,¹³ and cadmium, copper and silver amalgams.¹⁴



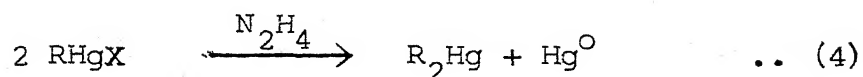
Sodium stannite¹⁵⁻¹⁷ has been widely used as a reducing agent for organomercuric halides giving excellent yield of products. The diorganomercury compounds are generally stable to further reduction or they are reduced slowly. Traylor and Winstein¹⁸ have examined the stereochemical course of symmetrization by sodium stannite, of several alkylmercuric halides. The evidence obtained by them leads to the mechanism outlined in Scheme V.3:

SCHEME V.3

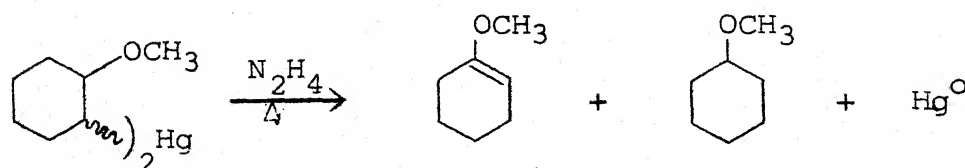
The structure of the intermediate $[\text{R}_2\text{HgBr}]^\bullet$ has been postulated as a resonance hybrid (Eq. 3):



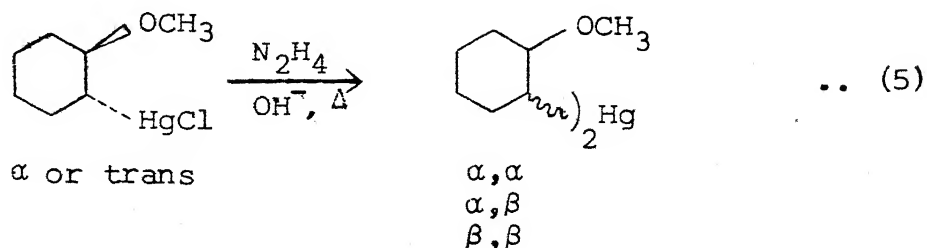
The formation of diorganomercurials by the treatment of organomercuric halides with hydrazine (Eq. 4) was first noted by Gilman and Wright¹⁹ and this reaction has since been widely used.²⁰



It has been established now that further reduction of the diorganomercury formed in Eq. 4, may also occur, with the formation of hydrocarbon and olefinic products²¹ shown below:

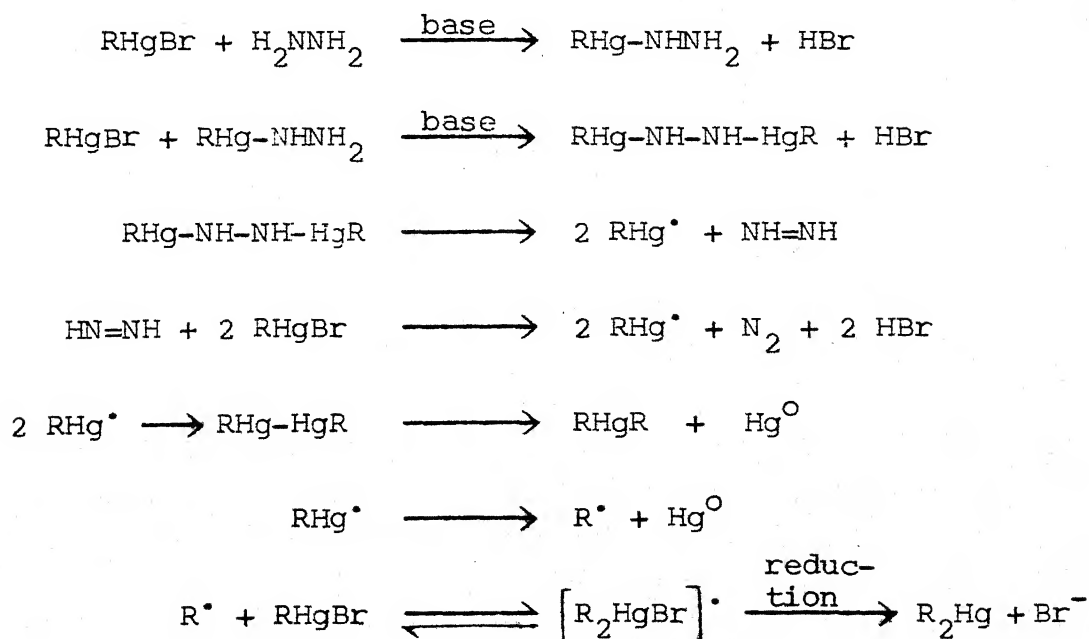


Reaction of a single diastereomer of 2-methoxycyclohexylmercuric chloride with hydrazine gives rise to a mixture of diastereomeric dialkylmercury products (Eq. 5):

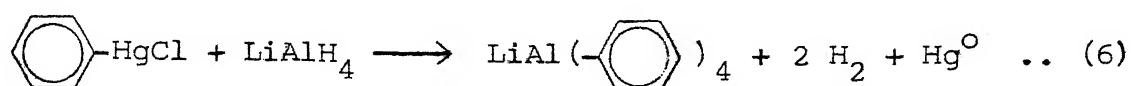


This lead Wright²¹ to postulate that free radicals are involved in the reduction of organomercuric halides with hydrazine. However, it was observed that hydrazine as such reduces organomercuric halides slowly but in the presence of an alkali, the reaction proceeds rapidly suggesting an (at least partially) ionic mechanism. To account for these observations, the mechanism outlined in scheme V.4 has been postulated:

SCHEME V.4



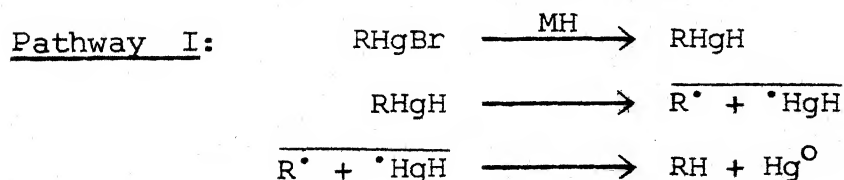
Winstein and Traylor²² demonstrated that lithium aluminium hydride (LAH) reduces organomercuric halides to hydrocarbons. Traylor²³ has postulated that an intermediate organoaluminium compound is formed in the reduction of phenylmercuric chloride with LAH; which on hydrolysis yields benzene (Eqs. 6 and 7):



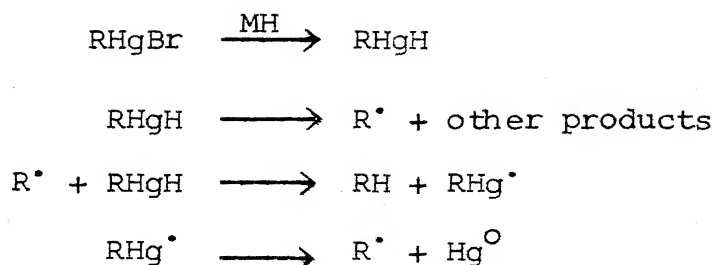
The fate of the halide ion in this reaction has not been discussed.

Free radical intermediates have been proposed in the reductive demercuration of alkylmercuric halides, by metal hydrides.²⁴⁻²⁶ The near constancy of the product distribution inspite of drastic changes in the nature of the metal hydrides used as reducing agents, has been taken in the literature²⁴ to suggest that these hydrides do not themselves donate hydrogen atoms to the intermediate alkyl radicals. Several metal hydrides e.g. sodium borohydride, diethylaluminium hydride, tri-n-butylphosphine copper(I) hydride, and tri-n-butyltin hydride, have been used. It has been proposed²⁴ that these reductions occur by either of the two pathways shown in Scheme V.5:

SCHEME V.5

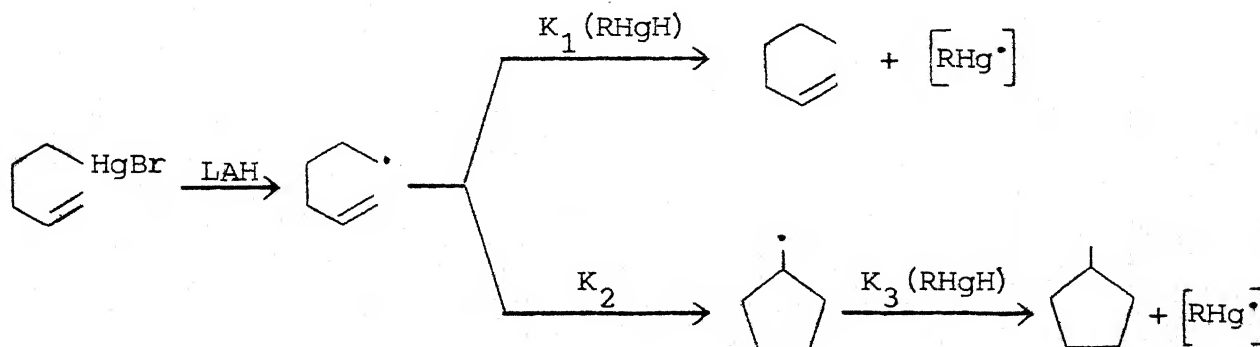


...contd.

Scheme V.5 (contd.)Pathway II:

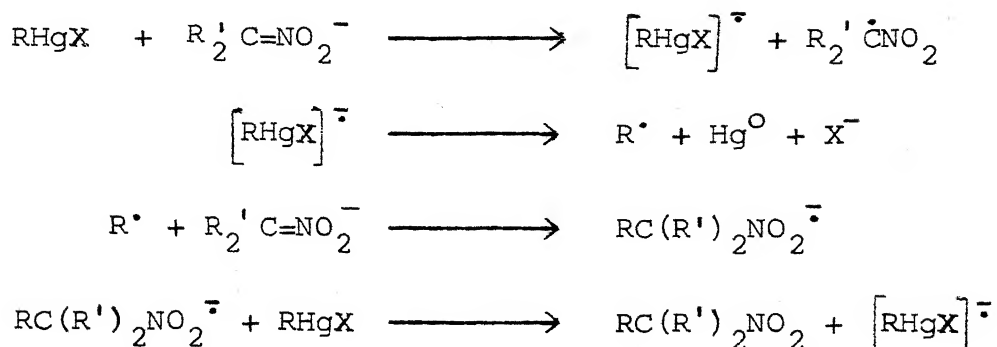
Evidence has not been presented to differentiate between the radical cage (pathway I) and radical chain (pathway II) mechanisms, but pathway II has been preferred, in view of the results obtained in the reductions of alkylmercuric bromides by NaBH_4 in the presence of oxygen.²⁷

The reactions of alkylmercuric halides with lithium aluminium hydride are also believed²⁸ to proceed via intervention of radicals. A mechanism similar to the one outlined in Scheme V.5 (pathway II) has been proposed for these reductions by LAH. Thus the reductive demercuration of hex-5-enyl-1-mercuric bromide by LAH has been postulated to proceed by the mechanism outlined in Scheme V.6:

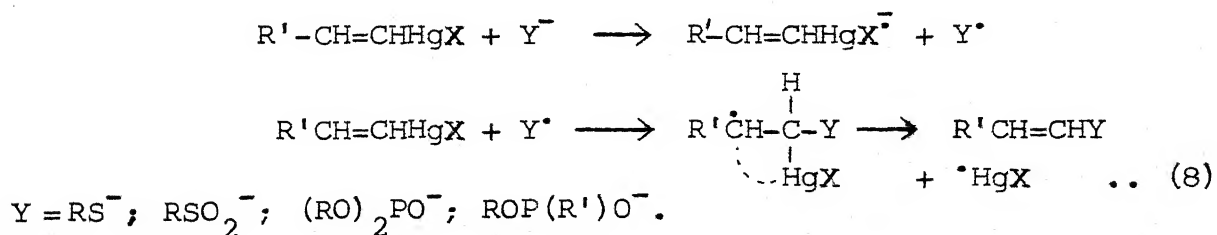
SCHEME V.6

Recently, Russell and coworkers²⁹ have demonstrated that alkylmercuric halides participate in the $S_{RN}1$ reaction with nitronate anions in Me_2SO or DMF (Scheme V.7):

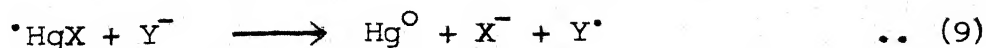
SCHEME V.7



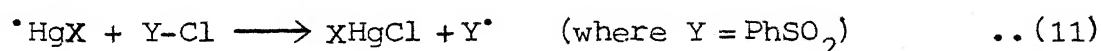
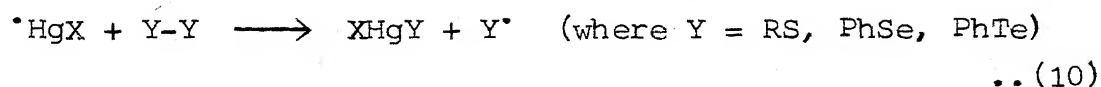
Vinylmercuric halides have been shown not to participate in a chain reaction with nitronate anions. However, it has been exhibited that vinylmercurials give radical chain substitution reactions with anions such as RS^- , RSO_2^- , $(RO)_2PO^-$, or $ROP(R')O^-$. According to Russell³⁰ these reactions involve an addition elimination process (Eq. 8); the initial formation of radicals presumably taking place by an electron transfer from the anion:



The chain is apparently propagated by the reaction of $\cdot HgX$ radical with the anion (Eq. 9):



Vinylmercurials are also known³¹ to undergo free radical chain substitution with RSSR, PhSeSePh, PhTeTePh or PhSO₂Cl. An addition elimination process similar to that shown in Eq. 8 has been proposed for these substitution reactions also. The propagation steps postulated for these reactions are shown in Eq. 10 and 11:



All these reactions are known to be stimulated by light and inhibited by radical scavengers.

In view of the facts that sodium naphthalene is an excellent source of electrons³²⁻³⁵ and lithium aluminium hydride can serve as a single electron as well as hydrogen atom donor,^{36,37} we decided to examine the details of the mechanistic roles of these two reagents in the reductive demercuration and symmetrization of some alkyl- and arylmercuric halides.

V.3 Results and Discussion

Reduction of organomercuric halides has been effected by a variety of reductants such as sodium metal,⁸ sodium stannite¹⁸ and hydrazine;²¹ but the mechanistic details of these reactions are obscure. Though, naphthalene radical anion is known to reduce arenediazonium cations³⁸ and certain benzylic halides³⁹

via $\pi^* \rightarrow \pi^*$ electron transfer pathways, its reaction with organomercuric halides has not been reported in the literature.

Occurrence of a new electron transfer mechanism involving radical intermediates in the uncatalyzed lithium aluminium hydride reduction of Z 2-chlorostilbene³⁶ and certain benzylic halides³⁷ has been recently demonstrated in our laboratory. Though radicals have been assumed²⁸ to intervene in the reduction of alkylmercuric halides with lithium aluminium hydride, the mode of formation of these intermediates is not understood.²⁴ In view of these facts, we have examined the reactions of a few organomercuric halides with sodium naphthalene as well as lithium aluminium hydride to elucidate the relevant reaction pathways.

The reactions of benzylmercuric chloride Ia, phenylmercuric chloride Ib, p-tolylmercuric chloride Ic and p-nitrophenylmercuric chloride Id with varying amounts of sodium naphthalene in THF solvent at 30°C under nitrogen atmosphere gave the results summarized in the Table V.1. Besides the products listed in the Table V.1, an unestimated amount of metallic mercury was also obtained in these reactions. The reactions with equimolar amounts of sodium naphthalene in 30 min (runs 1, 8, 13 and 15) were largely incomplete; but on increasing the reaction time, more of the organomercuric chloride I reacted in each case. The reactions of benzylmercuric chloride, phenylmercuric chloride and p-nitrophenylmercuric chloride were complete in 30 min with twice the molar quantities of sodium naphthalene, but only 88% of p-tolylmercuric chloride reacted

TABLE V.1: Reactions^a of Organomercuric Halides I with Sodium Naphthalene

Run	Organo- mercuric halide: R-Hg-Cl, <u>I</u>	Molar ratio $C_{10}H_8^- : \underline{I}$	Reac- tion time (min)	% Yield of Products ^b				
				R-Hg-R	R-H	R-R	Naphth- alene ^c	Starting halide <u>I</u>
1	<u>Ia</u>	1.00	30	21	2	9	85	69
2	<u>Ia</u>	1.00	360	24	3	12	89	62
3	<u>Ia</u>	2.00	30	46	30	16	90	-
4 ^d	<u>Ia</u>	1.00	30	13	2	5	92	78
5 ^d	<u>Ia</u>	2.00	30	41	26	13	90	12
6 ^e	<u>Ia</u>	2.00	30	6	46	3	87	31
7 ^f	<u>Ia</u>	1.00	30	20	2	8	89	67
8	<u>Ib</u>	1.00	30	32	12	3	88	51
9	<u>Ib</u>	1.00	360	36	14	3	93	45
10	<u>Ib</u>	2.00	30	53	38	2	92	-
11 ^d	<u>Ib</u>	1.00	30	24	8	2	90	60
12 ^f	<u>Ib</u>	1.00	30	31	10	3	90	53
13	<u>Ic</u>	1.00	30	23	6	2	85	70
14	<u>Ic</u>	2.00	30	45	36	2	91	12
15 ^g	<u>Id</u>	1.00	30	33	3	2	90	35
16 ^g	<u>Id</u>	2.00	30	31	29	2	84	-

a, 5×10^{-3} mol of R-Hg-Cl were reacted with $Na^+C_{10}H_8^-$ in THF, at 30°C, under nitrogen atmosphere; Ia = $C_6H_5CH_2-Hg-Cl$, Ib = $C_6H_5-Hg-Cl$, Ic = $p-H_3C-C_6H_4-Hg-Cl$, Id = $p-O_2N-C_6H_4-Hg-Cl$.

b, Percentage based on organomercuric halides, unless otherwise stated. An unestimated amount of metallic mercury was also obtained in these reactions. Mercury was separated from other products during work up by filtration through celite.

c, Percentage based on sodium naphthalene.

d, In the presence of 5×10^{-3} mol naphthalene added from outside. Yield of naphthalene based on the total amount of naphthalene, obtainable from initially used $Na^+C_{10}H_8^-$ as well as $C_{10}H_8$ added from outside.

e, In the presence of cumene (0.1 mol).

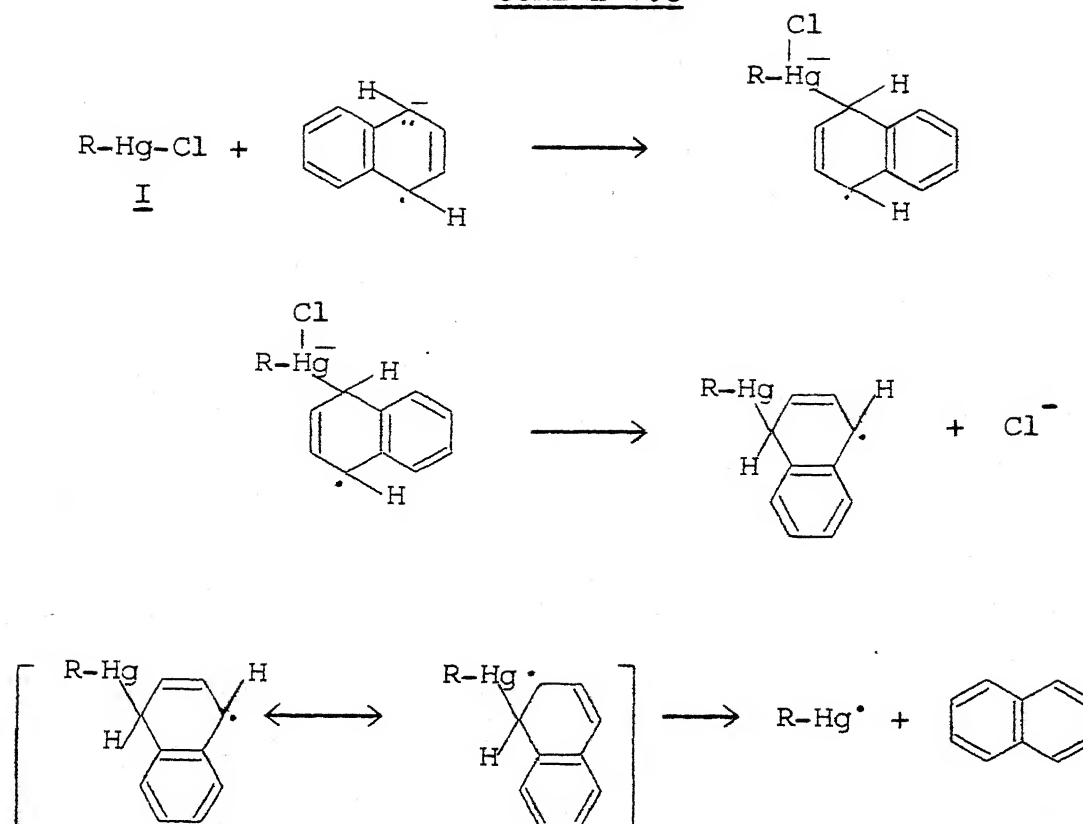
f, In the presence of $MgBr_2$ (0.01 mol). On subsequent reaction with benzophenone, not even a trace of benzylidiphenylcarbinol in run 7 and triphenylcarbinol in run 12, was detected.

g, Unestimated amounts of azobenzene and azoxybenzene were also obtained. Additional mixture of colored products could not be analyzed.

under similar conditions. The conceivable formation of benzyl anions in the reaction of benzylmercuric chloride and of aryl anions in the reactions of different arylmercuric chlorides, with equimolar quantities of sodium naphthalene is ruled out in view of our inability to trap these species in separate control experiments. Thus, the reactions of benzylmercuric chloride and phenylmercuric chloride with equimolar amounts of sodium naphthalene in the presence of MgBr_2 , on subsequent reaction with benzophenone, did not yield even traces of benzyldiphenylcarbinol and triphenylcarbinol, respectively. It is evident from the observed product distribution that the symmetrization of organomercuric chlorides predominates over demercuration, but this trend is reversed in the presence of cumene. All these facts coupled with the observed formation of dimeric hydrocarbons in these reactions, become discernible if intervention of radicals is visualized in these reactions.

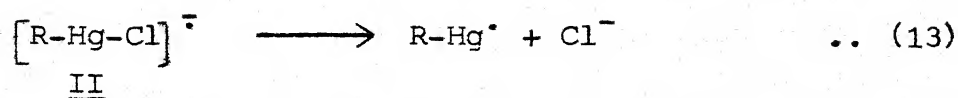
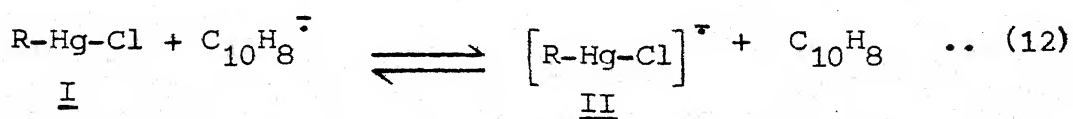
An attractive possibility for the formation of radicals is the nucleophilic displacement of Cl^- by naphthalene radical anion on the electrophilic mercury of organomercuric chloride I, followed by homolytic cleavage of the C-Hg bond into R-Hg^\bullet radicals and naphthalene, as shown in Scheme V.8. That this pathway for the formation of radicals is unlikely, was proved when the reaction of phenylmercuric chloride with 9-fluorenyl anion, an equally good nucleophile vis a vis naphthalene radical anion, did not yield the expected fluorenylphenylmercury, though the latter compound is stable under our reaction conditions.

SCHEME V.8

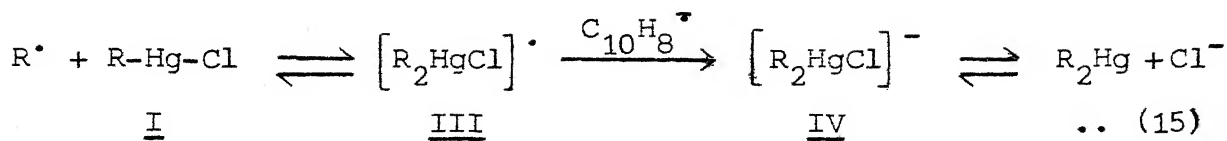
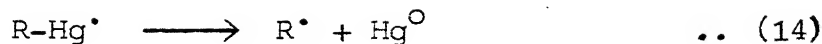


In view of the known electron donating ability^{38,39} of naphthalene radical anion towards appropriate substrates and the fact that organomercuric halides accept electrons even from relatively weaker reducing agents²⁹ (see section V.2), we propose the occurrence of an electron transfer free radical mechanism outlined in Scheme V.9 to rationalize all the observations recorded for these reactions.

SCHEME V.9

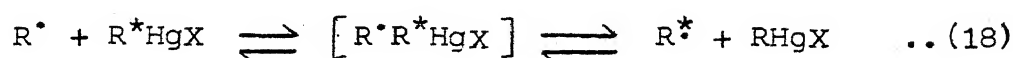


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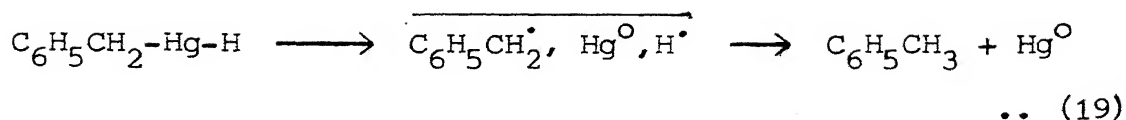
Scheme V.9 (contd.)

The reaction is initiated by the transfer of an electron from the π^* MO of naphthalene radical anion to the lowest unoccupied molecular orbital (LUMO) of organomercuric chloride I. The reversibility of step 12 is evident from the observed retardation of the reactions of benzylmercuric chloride and phenylmercuric chloride with sodium naphthalene in the presence of naphthalene added from outside (runs 4, 5 and 11). It is obvious that in the presence of added naphthalene, the equilibrium shown in step 12 would shift towards the left, thus explaining the recovery of larger amounts of unreacted starting materials in runs 4, 5 and 11 compared to runs 1, 3 and 8, respectively. The fragmentation of radical anion II into the organomercury radical R-Hg^\bullet and Cl^- is favored by the high electronegativity of Cl and has been established by electrochemical⁵ and polarographic⁶ reduction studies on similar substrates. The decomposition of the radical R-Hg^\bullet to yield the radical R^\bullet and metallic mercury is known⁴⁰ to be rapid at our reaction temperature. The bond dissociation energy for R-Hg^\bullet , where R = alkyl,

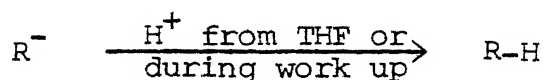
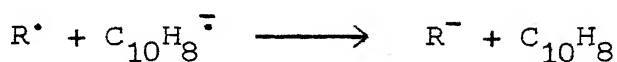
is very small, varying from 0 - 6 kcal/mol.⁴⁰ The R^\bullet radical may then add to organomercuric halide I, giving an adduct III,^{40,41} which on acceptance of an electron from naphthalene radical anion would yield the symmetrical diorganomercurial $R-Hg-R$ (step 15), abstract a hydrogen atom from the solvent to produce the hydrocarbon $R-H$ (step 16) or dimerize to form $R-R$ (step 17). The reversible formation of the electron deficient species $[R_2HgCl]^\bullet$ has also been previously proposed in the literature^{41,42} to account for the racemization, or interconversion of organomercurials by alkyl or aryl radicals (Eq. 18):



Anion IV formed in step 15, may undergo reversible cleavage of the $Hg-Cl$ bond; but it is known⁴³ not to fragment into organomercuric chloride I and R^- anion by the heterolytic cleavage of the $R-Hg$ bond. As cumene donates a hydrogen atom to R^\bullet radical with ease, the observed increase in the yields of toluene at the expense of dibenzylmercury and bibenzyl in run 6, established the formation of these products via the benzyl radical $C_6H_5CH_2^\bullet$. Since the $C-H$ bond strength⁴⁴ (79 kcal/mol for the benzylic $C-H$ bond) is much greater than the $Hg-H$ bond strength⁴⁴ (9.5 kcal/mol), the hydrogen atom abstraction by $R-Hg^\bullet$ radical from cumene to yield $R-Hg-H$ is highly unlikely. Thus, the possible formation of toluene via fragmentation²⁴ of $C_6H_5CH_2-Hg-H$ in a solvent cage (Eq. 19) is ruled out.

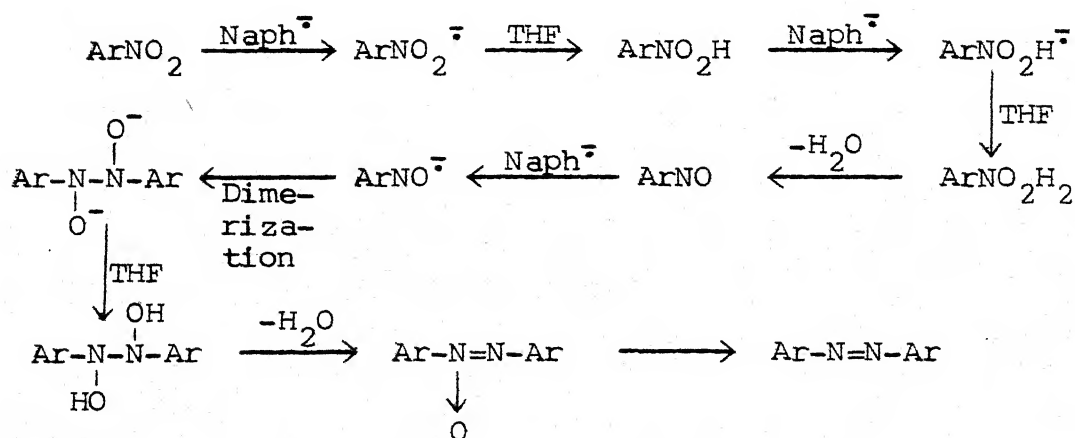


Alkyl or aryl anions may be formed from the corresponding radicals in the presence of an excess of naphthalene radical anion. This is in agreement with the observed increase in the yields of monomeric hydrocarbons R-H, in the reactions of organo-mercuric chlorides carried out with twice the molar quantities of sodium naphthalene (runs 3, 10, 14 and 16).



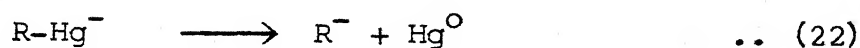
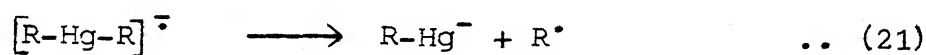
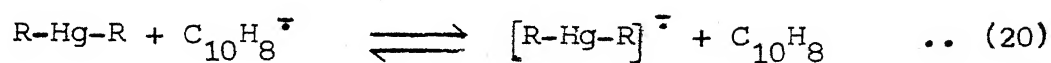
Small amounts of azobenzene and azoxybenzene formed in the reactions of p-nitrophenylmercuric chloride Id (runs 15 and 16) may arise by the subsequent electron transfer reduction of nitrobenzene, formed in these reactions, by sodium naphthalene. The essential steps of this mechanism as proposed earlier by Holy⁴⁵ are outlined in Scheme V.10:

SCHEME V.10



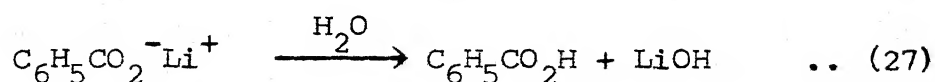
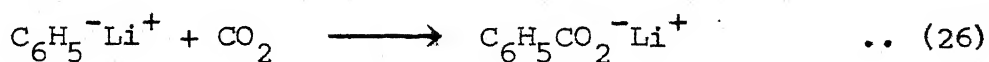
The diorganomercurials formed in these reactions may also be reduced, though more slowly, by a similar electron transfer from naphthalene radical anion. Indeed, our initial experiments on the reaction of dibenzylmercury with sodium naphthalene have indicated the formation of toluene, bibenzyl and metallic mercury. A tentative mechanism proposed for these reactions is outlined in Scheme V.11:

SCHEME V.11



The occurrence of an electron transfer free radical mechanism has also been demonstrated in the lithium aluminium hydride reductions of benzylmercuric chloride Ia, phenylmercuric chloride Ib, p-tolylmercuric chloride Ic and p-nitrophenylmercuric chloride Id. On the addition of lithium aluminium hydride contained in dry THF solvent (see Sec. V.4) at 30°C under dry nitrogen atmosphere with magnetic stirring, the reaction commenced with the evolution of hydrogen gas and simultaneous separation of metallic mercury. The

reaction mixtures in different runs, on work up, gave the results summarized in Table V.2. An earlier suggestion,²² favoring the formation of an intermediate organoaluminium compound in the reaction of lithium aluminium hydride with phenylmercuric chloride, which accounts for the formation, after work up, of benzene is untenable since the amount of benzene in the reaction mixture, estimated in run 6 before and after work up, was found to remain essentially the same. Furthermore, such a process would not explain the formation of diorganomercurials R-Hg-R, and dimeric products R-R, obtained in these reactions. The absence of highly nucleophilic phenyllithium in the lithium aluminium hydride reduction of phenylmercuric chloride has been demonstrated by Traylor²³ who found that in the presence of carbon dioxide no benzoic acid was formed, though this product should be expected by the trapping of the phenyl anion with CO₂ (Eqs. 26 and 27), if such an anionic intermediate was formed in these reactions:



It is evident from the product distribution listed in Table V.2 that symmetrization of the organomercuric chlorides predominates over reductive demercuration, but this trend is reversed in the presence of cumene (run 5). These arguments coupled with an earlier observation²⁸ indicating the intermediacy of alkyl radicals in the reductive demercuration of

TABLE V.2: Reactions^a of Organomercuric Halides I with LiAlH₄

Run	Organo- mercuric halide, <u>I</u> 0.005 mol	LiAlH ₄ mol	Reac- tion time, min	% Yield of Products ^b				H ₂ ^c ml
				R-Hg-R	R-R	R-H	Starting material <u>I</u>	
1	<u>Ia</u>	0.005	30	53	11	25	-	53
2	<u>Ia</u>	0.0025	30	55	13	14	12	49
3	<u>Ia</u>	0.00125	30	50	10	8	26	30
4	<u>Ia</u>	0.00125	300	52	14	10	17	33
5 ^d	<u>Ia</u>	0.00125	30	8	2	39	48	36
6	<u>Ib</u>	0.005	30	58	2	32 ^e	-	54
7	<u>Ib</u>	0.0025	30	60	2	26	11	48
8	<u>Ib</u>	0.00125	30	55	3	16	25	31
9	<u>Ib</u>	0.00125	300	57	3	18	17	33
10 ^f	<u>Ib</u>	0.005	30	37	2	23	28	57
11	<u>Ic</u>	0.005	30	41	2	20	26	40
12	<u>Ic</u>	0.0025	30	38	2	16	31	35
13	<u>Ic</u>	0.00125	30	33	2	10	40	21
14 ^g	<u>Id</u>	0.0025	30	45	3	21	5	51
15 ^g	<u>Id</u>	0.00125	30	42	3	10	19	37

a, Reactions conducted in THF (60 ml) at 30°C under dry nitrogen; Ia = C₆H₅CH₂-Hg-Cl, Ib = C₆H₅-Hg-Cl, Ic = p-H₃C-C₆H₄-Hg-Cl, Id = p-O₂N-C₆H₄-Hg-Cl.

b, Percentage yields based on R-Hg-Cl, I. An unestimated amount of metallic mercury was also obtained.

c, Volume of H₂ was determined at atmospheric pressure by comparison with H₂ control experiment in the absence of I using same batch of reactants and solvent under identical conditions.

d, In presence of cumene (0.1 mol).

e, Yield remained essentially unaltered on estimation before and after work up of the reaction mixture.

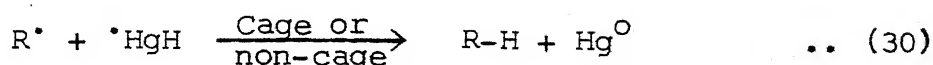
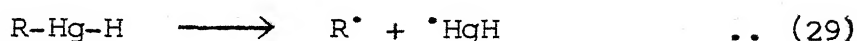
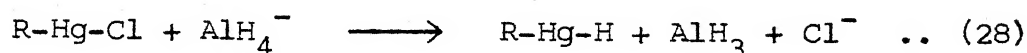
f, In presence of naphthalene (0.005 mol). Naphthalene was recovered back unchanged after the reaction.

g, Unestimated amounts of azobenzene and azoxybenzene were also obtained. Additional colored product mixture could not be analyzed.

alkylmercuric halides by lithium aluminium hydride, establish that radicals are effective intermediates in the reactions of benzylmercuric chloride, as well as phenylmercuric chloride, p-tolylmercuric chloride and p-nitrophenylmercuric chloride, with lithium aluminium hydride.

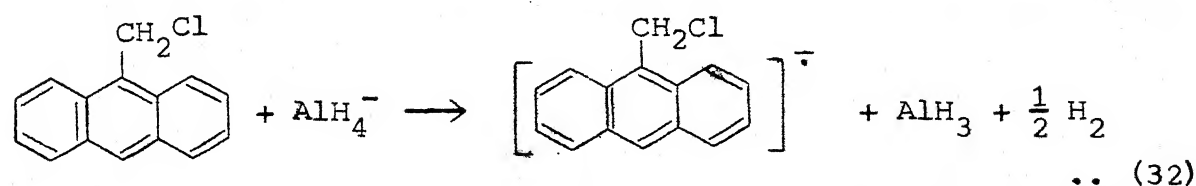
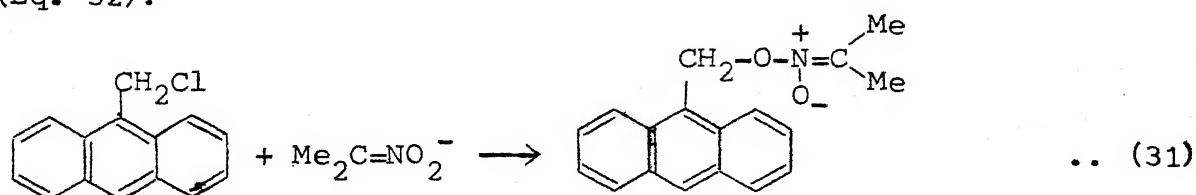
A conceivable pathway^{24, 27} for the production of radicals in these reactions is the nucleophilic attack of the hydride anion on the electrophilic mercury of organomercuric chloride I, resulting in the intermediate organomercuric hydride R-Hg-H, followed by homolysis of the carbon-mercury bond as shown in Scheme V.12:

SCHEME V.12



Such a hydride transfer mechanism is untenable in our reactions, in view of the observed retardation of the reaction of phenylmercuric chloride with LiAlH_4 in the presence of naphthalene. Since in a separate control experiment, naphthalene has been shown not to react with lithium aluminium hydride, it would not be expected to interfere in the reaction pathway elucidated in Scheme V.12. Thus, this pathway for the formation of radicals in these reactions is ruled out. Furthermore, the Al-H bond energy⁴⁴ (68 kcal/mol) is considerably higher than the Hg-H

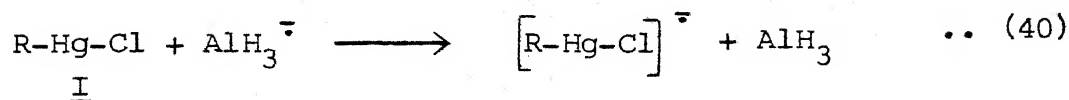
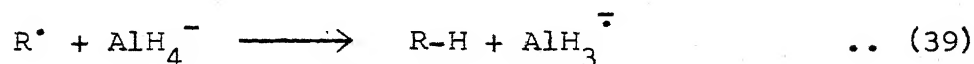
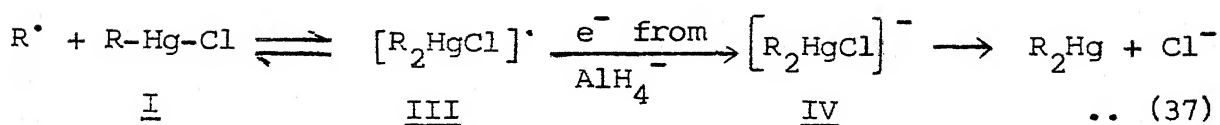
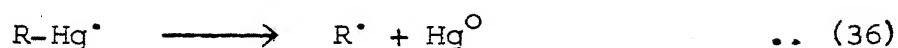
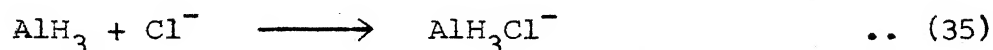
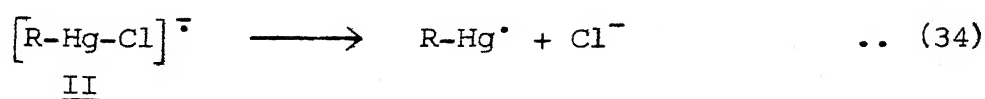
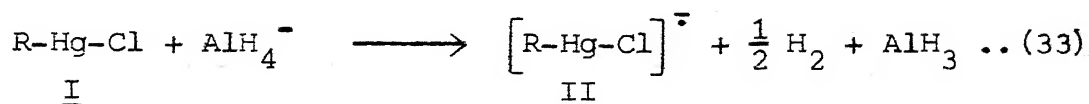
bond energy⁴⁴ (9.5 kcal/mol) and thus the formation of R-Hg-H in Eq. 28 itself is unlikely in view of the endothermicity of the overall reaction reflecting unfavorable energetics. Thus, homolysis of the Hg-H bond in hypothetical R-Hg-H as a means of hydrogen gas evolution is also considered imaginary. Electron transfer from lithium aluminium hydride to the organomercuric halide I, on the other hand, is quite feasible as the 2-nitropropanate anion which is known to be inferior to lithium aluminium hydride as electron donor towards 9-chloromethylanthracene,^{37,46} readily transfers an electron to alkylmercuric chlorides.²⁹ Though 2-nitropropanate anion reacts with 9-chloromethylanthracene by an S_N2 displacement process⁴⁶ outlined in Eq. 31, lithium aluminium hydride reduces 9-chloromethylanthracene by the transfer of an electron from the AlH₄⁻ anion³⁷ (Eq. 32):



In view of the foregoing arguments, we conclude that the reactions of organomercuric halides with lithium aluminium hydride are triggered off by a fast electron transfer³⁷ from

AlH_4^- to the lowest ABMO of organomercuric halide I, producing radical anion II, hydrogen and AlH_3 , as shown in step 33 of the Scheme V.13:

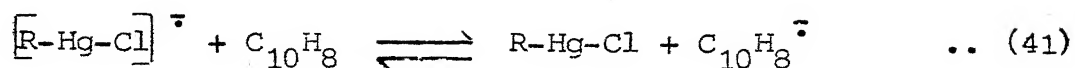
SCHEME V.13



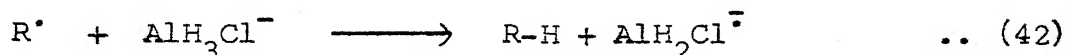
The radical anion II, formed in step 33, fragments to yield the highly unstable radical R-Hg^\bullet and Cl^- ion.^{5,6} The decomposition of the radical R-Hg^\bullet to yield the radical R^\bullet and metallic mercury is known⁴⁰ to be rapid at our reaction temperature. The R^\bullet radical may then add to organomercuric chloride I giving an electron deficient adduct III, which on acceptance of an electron from AlH_4^- would fragment^{40,41} into Cl^- and diorganomercurial R-Hg-R side by side. Radical R^\bullet may also dimerize to yield R-R

or abstract a hydrogen atom from AlH_4^- to yield the hydrocarbon R-H and AlH_3^- . Anion IV is not formed by the addition of Cl^- to R_2Hg in these reactions due to the removal of Cl^- by complexation with AlH_3 (step 35). Abstraction of a hydrogen atom by an alkyl radical or aryl radical from AlH_4^- is precedented.^{36, 37} It is evident from the yields of various products obtained in these reactions that the abstraction of a hydrogen atom by the radical R^\bullet to yield the hydrocarbon R-H (step 39), is a slow process as compared to the addition of this radical to the organomercuric chloride and subsequent reduction of the adduct $[\text{R}_2\text{HgCl}]^\bullet$ giving the diorganomercurial R-Hg-R . However, as the amount of lithium aluminium hydride is increased, step 39 also becomes significant, resulting in a dramatic increase in the yields of monomeric hydrocarbons R-H . The AlH_3^- generated in step 39; effectively competes with AlH_4^- in electron donation to the organomercuric chloride. Generation of and electron donation by AlH_3^- is evident from the fact that the volume of hydrogen gas actually evolved in these reactions in accordance with step 33 is much less than the amount of organomercuric chloride consumed. Abstraction of a hydrogen atom by the benzyl radical $\text{C}_6\text{H}_5\text{CH}_2^\bullet$ from cumene, a good hydrogen atom donor to radicals, results in an enhanced yield of toluene in run 5 at the expense of dibenzylmercury and bibenzyl. The retardation of the reaction in the presence of naphthalene as observed in the reaction of phenylmercuric chloride (run 10) is rationalized in terms of the equilibrium illustrated in Eq. 41,

existence of which has been demonstrated in the reactions of organomercuric chlorides with sodium naphthalene discussed earlier:



The anion AlH_3Cl^- , formed in step (35) may also donate a hydrogen atom to the radical R^{\cdot} , yielding radical anion $\text{AlH}_2\text{Cl}^{\cdot-}$ (Eq. 42):



The ion AlH_3Cl^- and the radical anion $\text{AlH}_2\text{Cl}^{\cdot-}$ can also donate electrons to the organomercuric chlorides I, as inferior alternatives to AlH_4^- and $\text{AlH}_3^{\cdot-}$, respectively. Similarly, ions $\text{AlH}_2\text{Cl}_2^-$, AlHCl_3^- and AlCl_4^- may also be formed in the medium in succession. The first two of these would act as hydrogen atom donors producing radical anions, $\text{AlHCl}_2^{\cdot-}$ and $\text{AlCl}_3^{\cdot-}$, respectively. These ions $\text{AlH}_2\text{Cl}_2^-$, AlHCl_3^- , AlCl_4^- and radical anions $\text{AlHCl}_2^{\cdot-}$ and $\text{AlCl}_3^{\cdot-}$ may also donate electrons to organomercuric chlorides I. The recovery of lesser amounts of unreacted, starting organomercuric chlorides, on increasing the reaction time in runs 4 and 9, is in conformity with the expected order of efficiency³⁷ in reactivities of alanates and alane radical anions, which is as follows:

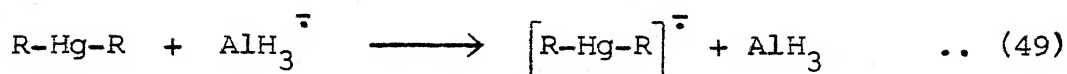
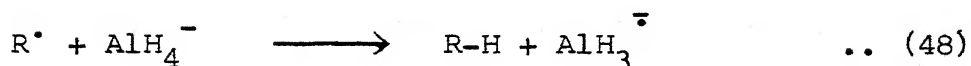
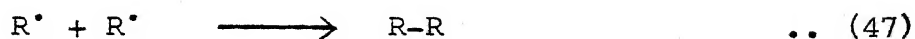
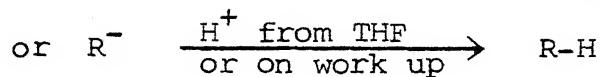
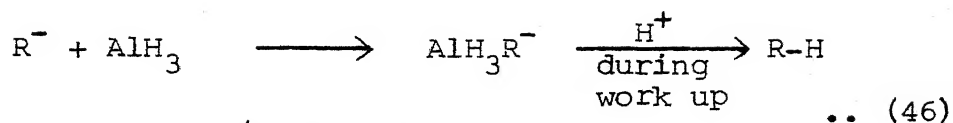
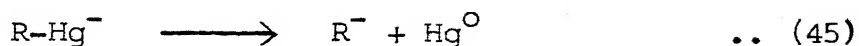
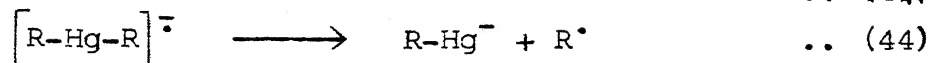
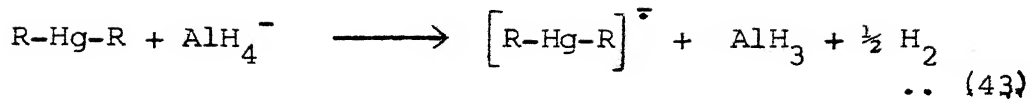
As electron donor: $\text{AlH}_4^- > \text{AlH}_3\text{Cl}^- > \text{AlH}_2\text{Cl}_2^- > \text{AlHCl}_3^- > \text{AlCl}_4^-$
 $\text{AlH}_3^{\cdot-} > \text{AlH}_2\text{Cl}^{\cdot-} > \text{AlHCl}_2^{\cdot-} > \text{AlCl}_3^{\cdot-}$.

As hydrogen donor: $\text{AlH}_4^- > \text{AlH}_3\text{Cl}^- > \text{AlH}_2\text{Cl}_2^- > \text{AlHCl}_3^-$.

Small amounts of azoxybenzene and azobenzene obtained in the reactions of p-nitrophenylmercuric chloride with lithium aluminium hydride, may arise by the partial reduction of nitrobenzene by an electron transfer mechanism similar to that proposed in Scheme V.10 earlier. Nitroaromatics are known to be reduced to the corresponding azoxyarenes and azoarenes by sodium borohydride,⁴⁷ alkoxides⁴⁸ and sodium naphthalene.⁴⁵

The mechanism elucidated in Scheme V.13 is also consistent with the reported²⁸ reductive demercuration and cyclization of 5-hexenylmercuric chloride with lithium aluminium hydride. Since both AlH_4^- and BH_4^- are known^{36,49} to transfer hydrogen atoms to radicals, the near agreement in deuterium isotope effects obtained for the LiAlH_4 and NaBH_4 reductions of this mercurial may be accounted for, without invoking the hydrogen atom transfer from the hypothetical alkylmercuric hydride (R-Hg-H).

The diorganomercurials formed in these reactions of organomercuric halides with lithium aluminium hydride, may be reduced further by an electron transfer process, though more slowly than the organomercuric halide I. Indeed, it has been observed by us that the reaction of dibenzylmercury with an equimolar amount of lithium aluminium hydride yields toluene, bibenzyl, metallic mercury and hydrogen gas and that only the first hydrogen in lithium aluminium hydride is involved in the reaction. The tentative mechanism proposed by us for these reductions is outlined in Scheme V.14:

SCHEME V.14

Further work is required to establish the role of AlH_3R^- as a possible electron donating species in this reduction.

V.4 Experimental

All melting points were determined on a MEL-TEMP melting point apparatus. IR spectra were recorded on Perkin-Elmer model-580 spectrophotometer. The GLC analyses were carried out on a Chromatography and Instruments Company Model AC1-FI instrument using 10% SE-30 on Crom-P (85-100 M) column of 2 m length. Column chromatography was done using activated silica-gel (Acme's 100-200 M). Silica-gel (asc-India) was used for TLC analyses.

and fluorene (Fluka) were used after recrystallization.

Preparation of sodium naphthalene⁶⁰

A perfectly dry 3 neck 100 ml RB flask was mounted over a magnetic stirring base, fitted with a condenser, a gas passing adaptor, and a stopper. Naphthalene (0.64 g; 5×10^{-3} mol or 1.28 g; 0.01 mol) dissolved in dry THF (30 ml) was placed in the flask. The contents of the flask were maintained at 30°C (room temperature). Pure, dry nitrogen gas was bubbled through the solution with continuous stirring. Sodium metal (0.17 g; 0.0075 g-atom or 0.35 g; ca. 0.015 g-atom) cut into small pieces was added to the solution. The mixture was stirred rapidly in the beginning and slowly after the reaction commenced. The progress of the reaction was measured from time to time by removal of a small sample of solution from the reaction mixture and determination of its sodium naphthalene content after dilution with alcohol, by titration with standard hydrochloric acid using methyl red as indicator. The formation of sodium naphthalene (green colored solution) was complete in $1\frac{1}{2}$ hr for the lower quantity and in 3 hr for the higher quantity. Solution of sodium naphthalene was thus prepared freshly for every reaction.

1. Reactions of benzylmercuric chloride with sodium naphthalene at room temperature (30°C), under nitrogen atmosphere

(a) Reaction with equimolar amounts of benzylmercuric chloride and sodium naphthalene, reaction time - 30 min.

A solution of benzylmercuric chloride (1.633 g; 5×10^{-3} mol) in 30 ml dry THF was placed in a 3-neck 250 ml RB flask, provided

with a gas inlet tube, a pressure equalizing dropping funnel and a condenser connected to a mercury trap. The contents of the flask were flushed with dry nitrogen gas for 30 min under magnetic stirring. Sodium naphthalene (5×10^{-3} mol) prepared as above was added through the dropping funnel slowly, with continuous stirring. The solution turned greenish-grey in color, due to the precipitation of finely divided metallic mercury. The reaction was allowed to proceed upto a period of 30 min and the reaction mixture then added to a 1% solution of hydrochloric acid (200 ml). This solution was passed through a one inch column of celite to remove the precipitated mercury. Celite column was washed with further 100 ml of 1% hydrochloric acid and then with ether. The original solution together with the washings was then extracted with five 50 ml portions of ether. The ethereal extract was washed with water, dried over anhydrous MgSO_4 , filtered and concentrated carefully at room temperature under reduced pressure. The volume of the concentrated ethereal extract was made up to 50 ml and this mixture of products was analyzed by GLC using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length. The products were identified by comparison of their retention times with those of the authentic samples and their yields determined by comparison of the peak areas with those from equal aliquots of standard solutions of authentic samples in ether. The yields of various products identified were: toluene (2%) and naphthalene (85%). The reaction mixture was then chromatographed over a column of silica gel (100-200 M). Elution

of the column with petroleum ether (b.p. 60-80°C) yielded a mixture of bibenzyl and naphthalene. This mixture was dissolved in ether (50 ml) and analyzed by GLC as described above. The yields of the two products estimated were: naphthalene (85%) and bibenzyl (9%). Elution of the column with a mixture of petroleum ether (b.p. 60-80°C) and benzene in the ratio 3:1, yielded dibenzylmercury (0.2 g; ca. 21%); m.p. 110°C; lit.⁵⁴ m.p. 111°C. Further elution of the column with a mixture of petroleum ether (b.p. 60-80°C) and benzene in the ratio 1:1, yielded the unreacted benzylmercuric chloride (1.126 g; ca. 69%); m.p. 103°C; lit.⁵⁰ m.p. 104°C. The compounds were characterized by mixed melting point technique and comparison of their IR spectra with those of the authentic samples.

(b) Reaction with equimolar amounts of benzylmercuric chloride and sodium naphthalene; reaction time - 360 min

To a solution of benzylmercuric chloride (1.633 g; 5×10^{-3} mol) in 30 ml of dry THF under nitrogen atmosphere was added sodium naphthalene (5×10^{-3} mol) prepared in 30 ml of THF and the reaction allowed to proceed for 360 min. The mixture was worked up as described for the reaction 1(a). GLC analysis and separation of the mixture of products on silica gel column, as described for the previous reaction, yielded toluene (3%), naphthalene (89%), bibenzyl (12%), dibenzylmercury (0.229 g; ca. 24%) and unreacted benzylmercuric chloride (1.012 g; ca. 62%).

(c) Reaction of benzylmercuric chloride with sodium naphthalene in molar ratio - 1:2; reaction time - 30 min

To a solution of benzylmercuric chloride (1.633 g; 5×10^{-3} mol) in dry THF (30 ml), kept at room temperature under nitrogen atmosphere, was added sodium naphthalene (0.01 mol) prepared in 30 ml of THF. Reaction mixture was worked up in the usual manner after 30 min. Metallic mercury was removed by filtration through celite and the resulting reaction mixture extracted with ether (5 x 50 ml). The ethereal extract was washed with water, dried, filtered and concentrated in the usual manner. GLC analysis and separation of product mixture on silica gel (100-200 M) column, yielded toluene (30%), naphthalene (90%), bibenzyl (16%), and dibenzylmercury (0.439 g; ca. 46%). Not even a trace of the starting benzylmercuric halide was detected. The yield of naphthalene is based on sodium naphthalene used.

(d) Reaction with equimolar amount of benzylmercuric chloride and sodium naphthalene, in presence of one mole equivalent of naphthalene; reaction time - 30 min.

In a 3-neck RB flask mounted over a magnetic stirring base was placed benzylmercuric chloride (1.633 g; 5×10^{-3} mol) and naphthalene (0.64 g; 5×10^{-3} mol) in dry THF (30 ml). The system was flushed with dry nitrogen and sodium naphthalene (5×10^{-3} mol) prepared in 30 ml of THF was added through a pressure equalizing dropping funnel. The reaction was worked up after 30 min as described for the reaction 1(a). GLC analysis and column chromatography of the reaction mixture

in the usual manner, yielded, toluene (2%), naphthalene (92%; based on the total of the amounts added as sodium naphthalene and naphthalene), bibenzyl (5%), dibenzylmercury (0.124 g; ca. 13%) and unreacted benzylmercuric chloride (1.273 g; ca. 78%).

(e) Reaction of benzylmercuric chloride with sodium naphthalene in molar ratio - 1:2, in presence of naphthalene (one mole equivalent of benzylmercuric chloride); reaction time - 30 min

In a 3-neck 250 ml RB flask, benzylmercuric chloride (1.633 g; 5×10^{-3} mol) and naphthalene (0.64 g; 5×10^{-3} mol) in dry THF (30 ml) were placed. The flask was maintained at room temperature (30°C) and the contents flushed with nitrogen. Sodium naphthalene (0.01 mol) contained in 30 ml of THF was then added through a pressure equalizing dropping funnel. The reaction was worked up after 30 min as described for the reaction 1(a). GLC analysis and column chromatography of the reaction mixture, as described in the previous experiments, yielded toluene (26%), naphthalene (90%; based on the total amount added in the form of sodium naphthalene and as naphthalene), bibenzyl (13%), dibenzylmercury (0.392 g; ca. 41%) and unreacted benzylmercuric chloride (0.196 g; ca. 12%).

(f) Reaction of benzylmercuric chloride with sodium naphthalene in molar ratio - 1:2, in presence of cumene; reaction time - 30 min

A solution of benzylmercuric chloride (1.633 g; 5×10^{-3} mol) and cumene (12 g; 0.1 mol) in dry THF (30 ml) was placed in a 3-neck RB flask, mounted over a magnetic stirring base and

maintained at 30°C. The contents of the flask were flushed with dry nitrogen for 30 min and sodium naphthalene (0.01 mol) added through a pressure equalizing dropping funnel. The reaction mixture was worked up as usual after 30 min. On GLC analysis and separation of the products by column chromatography, the distribution of products were found to be: toluene (46%), naphthalene (87%), bibenzyl (3%), dibenzylmercury (0.057 g; ca. 6%) and benzylmercuric chloride (0.506 g; ca. 31%), besides an unestimated amount of cumene.

(g) Reaction with equimolar amounts of benzylmercuric chloride and sodium naphthalene, in presence of MgBr_2 and subsequent treatment with benzophenone

(i) Preparation of MgBr_2 : Magnesium (0.24 g; 0.01 g-atom) and THF (10 ml) were taken in a 3-neck flask equipped with a magnetic stirring device, a gas passing adapter, a condenser, and a pressure equalizing dropping funnel. The contents of the flask were kept under dry nitrogen atmosphere and 1,2-dibromoethane (1.88 g; 0.01 mol) in 20 ml of dry THF slowly added through the dropping funnel. After completing the addition, stirring was continued for 1 hr during which period MgBr_2 was formed.

(ii) Reaction of benzylmercuric chloride and sodium naphthalene in presence of MgBr_2 and subsequent treatment with benzophenone:
A solution of benzylmercuric chloride (1.633 g; 5×10^{-3} mol) in 20 ml of THF was added to the flask containing MgBr_2 , through the dropping funnel. Dry nitrogen gas was passed through this

mixture for 30 min. Sodium naphthalene (0.005 mol) contained in 30 ml of dry THF was added slowly to this reaction mixture and the contents of the flask stirred for 30 min, after which a solution of benzophenone (1.8 g; 0.01 mol) in 20 ml THF was added. The contents of the flask were stirred for 4 hr at room temperature. The mixture was then poured into 1% hydrochloric acid (200 ml) and worked up as usual. TLC analysis of the reaction mixture did not give any spot for benzyldiphenylcarbinol as established by comparison with an authentic sample. GLC analysis and column chromatography of the reaction mixture as usual, yielded toluene (2%), naphthalene (89%), bibenzyl (8%), benzophenone (1.78 g; ca. 99%), dibenzylmercury (0.19 g; ca. 20%) and benzylmercuric chloride (1.094 g; ca. 67%).

2. Reactions of phenylmercuric chloride with sodium naphthalene at room temperature (30°C) under nitrogen atmosphere

(a) Reaction with equimolar amounts of phenylmercuric chloride and sodium naphthalene; reaction time - 30 min

A solution of phenylmercuric chloride (1.563 g; 5×10^{-3} mol) in 30 ml of dry THF was placed in a 3-neck 250 ml RB flask. The contents of the flask were flushed with nitrogen for 30 min under magnetic stirring. Sodium naphthalene (5×10^{-3} mol) contained in 30 ml of THF was added through a pressure equalizing dropping funnel slowly, with continuous stirring. The reaction mixture was worked up after 30 min, as usual. GLC analysis of the reaction mixture using a 10% SE-30 on Crom-P (85-100 M) column of 2m length by the calibration method as described

for the reaction 1(a), yielded, benzene (12%), and naphthalene (88%). The reaction mixture was charged over a silica gel (100-200M) column. Elution with petroleum ether (b.p. 60-80°C) yielded a mixture of naphthalene and biphenyl, which on GLC analysis, yielded naphthalene (88%) and biphenyl (3%). Elution of the column with a mixture of petroleum ether (b.p. 60-80°C) and benzene in the ratio 3:1, yielded diphenylmercury (0.283 g; ca. 32%); m.p. 124°C; lit.⁵⁵ m.p. 125°C. Further elution of the column with a mixture of petroleum ether and benzene in the ratio 1:1, yielded the unreacted phenylmercuric chloride (0.797 g; ca. 51%); m.p. 256°C; lit.⁵¹ 258°C. The compounds were characterized by the mixed melting point technique, GLC and comparison of their IR spectra with those of the authentic samples.

(b) Reaction with equimolar amounts of phenylmercuric chloride and sodium naphthalene; reaction time - 360 min

To a solution of phenylmercuric chloride (1.563 g; 5×10^{-3} mol) in 30 ml of dry THF under nitrogen atmosphere was added sodium naphthalene (5×10^{-3} mol) prepared in 30 ml of THF and the reaction allowed to proceed for 360 min. The reaction was worked up as usual, by adding it to 1% hydrochloric acid. After filtration through celite, to remove precipitated mercury, the reaction mixture was extracted with ether (5 x 50 ml). The ethereal extract was washed with water, dried, filtered, and concentrated. GLC analysis and separation of the product mixture on a silica gel column yielded benzene (14%),

naphthalene (93%), biphenyl (3%), diphenylmercury (0.319 g; ca. 36%) and unreacted phenylmercuric chloride (0.703 g; ca. 45%).

(c) Reaction of phenylmercuric chloride with sodium naphthalene in molar ratio - 1:2; reaction time - 30 min

Sodium naphthalene (0.01 mol) prepared in 30 ml of THF was added to a solution of phenylmercuric chloride (1.563 g; 5×10^{-3} mol) in dry THF (30 ml) under nitrogen atmosphere at room temperature. The reaction mixture was worked up after 30 min, in the usual manner. Analysis of the mixture of products by GLC and separation by chromatography on a silica-gel column, yielded benzene (38%), naphthalene (92%), biphenyl (2%) and diphenylmercury (0.469 g; ca. 53%). Not even a trace of unreacted phenylmercuric chloride was obtained. The yield of naphthalene is based on sodium naphthalene.

(d) Reaction with equimolar amounts of phenylmercuric chloride and sodium naphthalene, in presence of MgBr_2 , to detect the possible formation of phenylanions

(i) Preparation of MgBr_2 : MgBr_2 was prepared from magnesium (0.24 g; 0.01 g-atom) and 1,2-dibromoethane (1.88 g; 0.01 mol) in 30 ml of THF as described in the reaction 1(g).

(ii) Reaction of phenylmercuric chloride and sodium naphthalene in presence of MgBr_2 and subsequent treatment with benzophenone:
A solution of phenylmercuric chloride (1.563 g ; $5 \times 10^{-3} \text{ mol}$) in 20 ml of THF was added to the flask containing MgBr_2 prepared

in the previous experiment. Dry nitrogen gas was passed through this mixture for 30 min. Sodium naphthalene (5×10^{-3} mol) contained in 30 ml of dry THF was added slowly to this reaction mixture and the contents of the flask stirred for 30 min, after which a solution of benzophenone (1.8 g; 0.01 mol) in 20 ml of THF was added. The contents of the flask were stirred for 4 hr. at room temperature. The mixture was then poured into 1% hydrochloric acid (200 ml) and worked up as usual. TLC analysis of the reaction mixture did not show the presence of triphenylcarbinol, as established by comparison with an authentic sample. GLC analysis and column chromatography of the reaction mixture in the usual manner, yielded benzene (10%), naphthalene (90%), biphenyl (3%), diphenylmercury (0.274 g; ca. 31%) unreacted phenylmercuric chloride (0.828 g; ca. 53%), and benzophenone (1.77 g; ca. 98%).

(e) Reaction with equimolar amounts of phenylmercuric chloride and sodium naphthalene, in presence of one mole equivalent of naphthalene; reaction time - 30 min

In a 3-neck 250 ml RB flask, mounted over a magnetic stirring base, was placed phenylmercuric chloride (1.563 g; 5×10^{-3} mol) and naphthalene (0.64 g; 5×10^{-3} mol) dissolved in 30 ml of dry THF. The reaction system was flushed with dry nitrogen and then, sodium naphthalene (5×10^{-3} mol) prepared in 30 ml of THF was added through a pressure equalizing dropping funnel. The reaction mixture was worked up after 30 min, in the usual manner. GLC analysis and column chromatography of the reaction

mixture as described in the reaction 2(a), yielded benzene (8%), naphthalene (90%; based on total amount added in the form of sodium naphthalene and as naphthalene), biphenyl (2%), diphenylmercury (0.212 g; ca. 24%) and unreacted phenylmercuric chloride (0.938 g; ca. 60%).

3. Reactions of p-tolylmercuric chloride with sodium naphthalene at room temperature (30°C) under nitrogen atmosphere

(a) Reaction with equimolar amounts of p-tolylmercuric chloride and sodium naphthalene; reaction time - 30 min

A solution of p-tolylmercuric chloride (1.633 g; 5×10^{-3} mol) in 30 ml of dry THF was placed in a 3-neck 250 ml RB flask. The contents of the flask were flushed with nitrogen for 30 min, under magnetic stirring. Sodium naphthalene (5×10^{-3} mol) in 30 ml of THF was added slowly, through a pressure equalizing dropping funnel, with continuous stirring. The reaction mixture was worked up after 30 min in the usual manner. GLC analysis of the reaction mixture, yielded toluene (6%) and naphthalene (85%). The reaction mixture was chromatographed over a silica-gel (100-200 M) column. Elution with petroleum-ether (b.p. 60-80°C) yielded a mixture of naphthalene and 4,4'-dimethyldiphenyl. GLC analysis of this mixture by the calibration method yielded naphthalene (85%) and 4,4'-dimethyldiphenyl (2%). Elution of the column with a mixture of petroleum ether (b.p. 60-80°C) and benzene in the ratio 3:1 yielded di-p-tolylmercury (0.22 g; ca. 23%); m.p. 235°C; lit.⁵⁵ m.p. 236°C. Further elution of

the column with petroleum ether and benzene mixture (1:1) yielded the unreacted p-tolylmercuric chloride (1.143 g; ca. 70%); m.p. 238°C; lit.⁵² m.p. 238-239°C. The compounds were characterized by the mixed melting point technique, GLC and comparison of their IR spectra with those of the authentic samples.

(b) Reaction of p-tolylmercuric chloride with sodium naphthalene in molar ratio - 1:2; reaction time - 30 min

To a solution of p-tolylmercuric chloride (1.633 g; 5×10^{-3} mol) in dry THF (30 ml), kept at room temperature (30°C) under nitrogen atmosphere, was added a solution of sodium naphthalene (0.01 mol) in 30 ml of THF. The reaction mixture was worked up as usual after 30 min. GLC analysis and separation of the mixture of products by column chromatography as described for the reaction 3(a) yielded toluene (36%), naphthalene (91%), 4,4'-dimethyldiphenyl (2%), di-p-tolylmercury (0.43 g; ca. 45%) and unreacted p-tolylmercuric chloride (0.196 g; ca. 12%).

4. Reactions of p-nitrophenylmercuric chloride with sodium naphthalene at room temperature (30°C) under nitrogen atmosphere

(a) Reaction with equimolar amounts of p-nitrophenylmercuric chloride and sodium naphthalene, reaction time - 30 min

In a 3-neck 250 ml RB flask, mounted over a magnetic stirring base, a solution of p-nitrophenylmercuric chloride (1.788 g; 5×10^{-3} mol) in 30 ml of dry THF, was placed. The contents of the flask were flushed with dry nitrogen for 30 min.

Sodium naphthalene (5×10^{-3} mol) contained in 30 ml of dry THF was added to the above solution, through a pressure equalizing dropping funnel, slowly with continuous stirring. The reaction mixture was worked up after 30 min in the usual manner. GLC analysis of the mixture of products using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length, by the calibration method, yielded, nitrobenzene (3%), naphthalene (90%) and 4,4'-dinitrodiphenyl (2%). The reaction mixture was chromatographed on a silica-gel (100-200 M) column. Elution of the column with petroleum ether (b.p. 60-80°C) yielded naphthalene (0.576 g; ca. 90%). Further elution of the column with the same solvent gave traces of azobenzene and azoxybenzene, identified by comparison on TLC with authentic samples. Elution of the column with a mixture of petroleum ether (b.p. 60-80°C) and benzene in the ratio 3:1, yielded nitrobenzene in small amounts. Further elution of the column with benzene yielded 4,4'-dinitrodiphenyl (0.012 g; ca. 2%). Elution of the column with a mixture of chloroform and ethylacetate in the ratio (9:1) yielded the unreacted p-nitrophenylmercuric chloride (0.626 g; ca. 35%); m.p. 263°C; lit.⁵² m.p. 265°C. Further elution of the column with a mixture of chloroform and ethylacetate in the ratio 1:1, yielded di-p-nitrophenylmercury (0.35 g; ca. 33%); m.p. 317°C; lit.⁵⁵ m.p. 320° C. Elution of the column with ethylacetate yielded a colored pasty material which could not be analyzed. The compounds were characterized by the mixed melting point technique, GLC, and comparison of their IR spectra with those of the authentic samples.

(b) Reaction of p-nitrophenylmercuric chloride with sodium naphthalene in molar ratio - 1:2, reaction time - 30 min

To a solution of p-nitrophenylmercuric chloride (1.788 g; 5×10^{-3} mol) in dry THF (30 ml), kept at room temperature (30°C) under nitrogen atmosphere, was added sodium naphthalene (0.01 mol) contained in 30 ml of THF. Reaction mixture was worked up after 30 min in the usual manner. GLC analysis and separation of the product mixture on silica-gel column, as described in the previous experiment, yielded nitrobenzene (29%), naphthalene (0.538 g; ca. 84%), 4,4'-dinitrodiphenyl (0.012 g; ca. 2%), di-p-nitrophenylmercury (0.329 g; ca. 31%) and traces of azobenzene and azoxybenzene. Not even a trace of the starting material could be detected. Additional colored materials could not be analyzed.

5. Reaction of phenylmercuric chloride with fluorenyllithium in equimolar amounts at room temperature under nitrogen atmosphere

(i) Preparation of fluorenyllithium:⁵³ In a 3-neck RB flask, provided with a gas inlet tube, a condenser connected to a mercury trap and a pressure equalizing dropping funnel, was placed a suspension of finely cut lithium wire (0.2 g; 0.029 g-atom) in 10 ml of dry THF. The contents of the flask were flushed with dry nitrogen for 30 min under magnetic stirring. A solution of fluorene (0.83 g; 5×10^{-3} mol) in 20 ml of dry THF was added through the dropping funnel in 1.5 hr, with continuous stirring. The reaction mixture was periodically cooled by a

water-bath during the addition. The color of the mixture changed from green to orange. After the addition was complete, the mixture was stirred for a further period of 50 minutes and filtered through a glass wool plug.

(ii) Reaction with equimolar amount of phenylmercuric chloride; reaction time - 30 min: To a solution of phenylmercuric chloride (1.563 g; 5×10^{-3} mol) in dry THF (30 ml), kept at room temperature under nitrogen atmosphere, was added fluorenyllithium (5×10^{-3} mol) contained in 30 ml of THF as prepared above. The reaction mixture was worked up in the usual manner after 30 min. GLC analysis of the product mixture, by the calibration method, yielded fluorene (81%), 9-phenylfluorene (4%), and bifluorenyl (10%), besides a trace of benzene. TLC analysis showed the presence of phenylfluorenyl mercury in a trace amount, identified by comparison of its R_f value with that of an authentic sample. Column chromatography of the reaction mixture, yielded diphenylmercury (0.08 g; ca. 9%) and unreacted phenylmercuric chloride (1.297 g; ca. 83%), besides a trace amount of bifluorenylidene. The compounds were characterized by GLC, TLC, comparison of their IR spectra with those of the authentic samples, and by mixed melting point technique.

6. Reactions of benzylmercuric chloride with lithium aluminium hydride (LAH) at room temperature (30°C) under initial nitrogen atmosphere

(a) Reaction with equimolar amounts of benzylmercuric chloride and LAH; reaction time - 30 min

In a 3-neck 250 ml RB flask mounted over a magnetic stirring base, with a magnet inside, and connected to a nitrogen gas cylinder through a purifier, to a gas collector through a mercury trap and to a pressure equalizing dropping funnel, was placed a solution of benzylmercuric chloride (1.633 g; 5×10^{-3} mol) in dry THF (30 ml). The solution was purged with nitrogen gas with continuous stirring. Lithium aluminium hydride (0.19 g; 5×10^{-3} mol) contained in dry THF (30 ml) was added through the dropping funnel. Hydrogen gas (53 ml as at NTP, after accounting for the gas evolved in a control experiment under identical reaction conditions) was evolved. The reaction mixture turned greenish-grey due to the precipitation of mercury in finely divided form. The reaction mixture was worked up, after 30 min, by the addition of distilled water (50 ml), followed by the addition of 2% hydrochloric acid (50 ml). The precipitated mercury was removed by the filtration of this reaction mixture through celite. The reaction mixture was extracted with five 50 ml portions of diethylether. The combined ethereal extracts were washed with water, dried over anhydrous MgSO_4 , filtered and concentrated carefully at room temperature under reduced pressure, to a volume of 50 ml. The crude mixture was then analyzed by GLC using a 10% SE-30 on Chrom-P (85-100 M) column of 2 m length, and the products identified by comparison of their retention times with those for the authentic samples. The product yields were

obtained by a comparison of the peak areas with those for the authentic samples. Toluene (25%) was identified to have formed, by this method. The reaction mixture was chromatographed over activated silica-gel (100-200 M) column. Elution with petroleum-ether (b.p. 60-80°C) yielded bibenzyl (0.05 g; ca. 11%); m.p. 52°C; lit. m.p. 52.5°C. Further elution of the column with a mixture of petroleum-ether (b.p. 60-80°C) and benzene in the ratio 3:1, yielded dibenzylmercury (0.506 g; 53%), m.p. 110°C; lit.⁵⁴ m.p. 111°C. Not even a trace of the starting benzylmercuric chloride was detected. The compounds were characterized by the mixed melting point technique, GLC and comparison of their IR spectra with those of the authentic samples.

(b) Reaction of benzylmercuric chloride with LAH in molar ratio - 2:1; reaction time - 30 min

Addition of LAH (0.1 g; 0.0025 mol) contained in 30 ml of dry THF to a solution of benzylmercuric chloride (1.633 g; 5×10^{-3} mol) in 30 ml of dry THF kept at room temperature (30°C) under nitrogen atmosphere, resulted in the evolution of 49 ml (as at NTP) of hydrogen gas. The reaction was worked up after 30 min in the usual manner. GLC analysis and separation of the product mixture by column chromatography as detailed in the reaction 6(a), yielded toluene (14%), bibenzyl (0.059 g; ca. 13%), dibenzylmercury (0.525 g; ca. 55%) and benzylmercuric chloride (0.196 g; ca. 12%).

(c) Reaction of benzylmercuric chloride with LAH in molar ratio - 4:1; reaction time - 30 min

The above reaction was repeated using LAH (0.05 g; 0.00125 mol) and benzylmercuric chloride (1.633 g; 5×10^{-3} mol) in a total of 60 ml of dry THF. Hydrogen gas (30 ml as at NTP) was evolved. The product distribution was determined to be: toluene (8%), bibenzyl (0.046 g; ca. 10%), dibenzylmercury (0.478 g; ca. 50%) and benzylmercuric chloride (0.424 g; ca. 26%).

(d) Reaction of benzylmercuric chloride with LAH in molar ratio - 4:1; reaction time - 300 min

LAH (0.05 g; 0.00125 mol) contained in 30 ml of THF was added to a solution of benzylmercuric chloride (1.633 g; 0.005 mol) in dry THF (30 ml) kept at room temperature, under nitrogen atmosphere. Reaction, which commenced immediately, was allowed to proceed for 300 min. Hydrogen gas (33 ml as at NTP) was evolved. Mixture was worked up in the usual manner and the products obtained on GLC analysis and separation by column chromatography were: toluene (10%), bibenzyl (0.064 g; ca. 14%), dibenzylmercury (0.497 g; ca. 52%) and unreacted benzylmercuric chloride (0.278 g; ca. 17%).

(e) Reaction of benzylmercuric chloride with LAH in molar ratio - 4:1; in presence of cumene; reaction time - 30 min

In a 3-neck flask mounted over a magnetic stirring base was placed benzylmercuric chloride (1.633 g; 5×10^{-3} mol) and cumene (12 g; 0.1 mol) dissolved in dry THF (30 ml). The system

was flushed with dry nitrogen and LAH (0.05 g; 0.00125 mol) contained in 30 ml of dry THF was added to the flask. Hydrogen gas (36 ml as at NTP) was evolved. The reaction was worked up in the usual manner. GLC analysis and separation of the products by column chromatography, yielded: toluene (39%), bibenzyl (2%), dibenzylmercury (0.076 g; ca. 8%) unreacted benzylmercuric chloride (0.784 g; ca. 48%) and an unestimated amount of cumene.

7. Reactions of phenylmercuric chloride and lithium aluminium hydride (LAH) at room temperature (30°C) under nitrogen atmosphere

(a) Reaction of phenylmercuric chloride with LAH in molar ratio - 1:1; reaction time - 30 min

To a solution of phenylmercuric chloride (1.563 g; 5×10^{-3} mol) in dry THF (30 ml), kept at room temperature under nitrogen atmosphere, was added LAH (0.19 g; 5×10^{-3} mol) contained in dry THF (30 ml). Hydrogen gas (54 ml as at NTP, after accounting for the gas evolved in a control experiment under similar conditions) was evolved. Reaction was allowed to proceed for 30 min, and then analyzed by GLC, before work up, when benzene (32%) was estimated. The reaction mixture was then worked up by the addition of water followed by dil. HCl. After filtration through celite, the reaction mixture was extracted with diethyl ether (5 x 50 ml). The ethereal extract was washed with water, dried (anhydrous MgSO_4), filtered and concentrated to a volume of 50 ml. GLC analysis using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length, by the calibration method, yielded benzene (32%)

and biphenyl (2%). Complete removal of the solvent gave a crude mixture, which on column chromatography over activated silica-gel column using petroleum-ether (b.p. 60-80°C) and benzene in the ratio 3:1 (v/v) as eluant gave diphenylmercury (0.513 g; ca. 58%); m.p. 124°C; lit.⁵⁵ m.p. 125°C. Not even a trace of unreacted phenylmercuric chloride was detected. Diphenylmercury, was characterized by the mixed melting point technique and comparison of its IR spectrum with that of an authentic sample.

(b) Reaction of phenylmercuric chloride with LAH in molar ratio-2:1; reaction time - 30 min

Reaction was carried out by adding LAH (0.1 g; 0.0025 mol) contained in dry THF (30 ml) to a solution of phenylmercuric chloride (1.563 g; 5×10^{-3} mol) in dry THF (30 ml) under nitrogen atmosphere. The reaction proceeded with the evolution of hydrogen gas (48 ml as at NTP) and the mixture was worked up after 30 min in the usual manner. GLC analysis and separation of the product mixture by column chromatography, in the manner described for the reaction 7(a), yielded benzene (26%), biphenyl (2%), dibenzylmercury (0.573 g; 60%) and unreacted phenylmercuric chloride (0.172 g; ca. 11%); m.p. 257°C; lit.⁵¹ m.p. 258°C. The compounds were identified by GLC, mixed melting point technique and comparison of their IR spectra with those of the authentic samples.

(c) Reaction of phenylmercuric chloride with LAH in molar ratio - 4:1; reaction time - 30 min

LAH (0.05 g; 0.00125 mol) contained in 30 ml of dry THF was added to a solution of phenylmercuric chloride (1.563 g; 5×10^{-3} mol)

in 30 ml of THF, under nitrogen atmosphere. Hydrogen gas (31 ml as at NTP) was evolved. The reaction mixture was worked up after 30 min in the usual manner. GLC analysis by calibration method and separation of the products using silica-gel column gave: benzene (16%), biphenyl (3%), diphenylmercury (0.525 g; ca. 55%) and unreacted phenylmercuric chloride (0.391 g; ca. 25%).

(d) Reaction of phenylmercuric chloride with LAH in molar ratio - 4:1; reaction time - 300 min

Reduction was carried out by the addition of LAH (0.05 g; 0.00125 mol) contained in dry THF (30 ml) to a solution of phenylmercuric chloride (1.563 g; 0.005 mol) in 30 ml of THF, under nitrogen atmosphere. Reaction was allowed to proceed for 300 min when 33 ml (as at NTP) of hydrogen gas evolved. The reaction mixture was worked up by addition of distilled water followed by acidified water. The products were extracted with ether and the ethereal extract washed, dried, filtered and concentrated to give a mixture, which was analyzed by GLC and separated by means of column chromatography in the manner described for the reaction 7(a). The products obtained were: benzene (18%), biphenyl (3%), diphenylmercury (0.544 g; ca. 57%) and phenylmercuric chloride (0.266 g; ca. 17%).

(e) Reaction of phenylmercuric chloride with LAH in molar ratio- 1:1, in presence of naphthalene; reaction time - 30 min

In a 3-neck RB flask mounted over a magnetic stirring base were placed phenylmercuric chloride (1.563 g; 0.005 mol) and

naphthalene (0.64 g; 0.005 mol) dissolved in 30 ml of dry THF. The reaction system was flushed with nitrogen and LAH (0.19 g; 0.005 mol) contained in 30 ml of dry THF was added to the flask. Hydrogen gas (57 ml as at NTP) was evolved. On work up, GLC analysis by the calibration method and separation of the products by column chromatography, the products were found to be: benzene (23%); naphthalene (ca. 100%), biphenyl (2%), diphenylmercury (0.353 g; ca. 37%) and unreacted phenylmercuric chloride (0.438 g; ca. 28%).

8. Reactions of p-tolylmercuric chloride with LAH, at room temperature under nitrogen atmosphere

(a) Reaction of p-tolylmercuric chloride with LAH in molar ratio - 1:1; reaction time - 30 min

LAH (0.19 g; 0.005 mol) contained in dry THF (30 ml) was added to a solution of p-tolylmercuric chloride (1.633 g; 0.005 mol) in 30 ml of dry THF kept at room temperature (30°C) under nitrogen atmosphere. Hydrogen gas (40 ml as at NTP, after accounting for the gas evolved in a control experiment under identical conditions) was evolved. Reaction was worked up after 30 min by the addition of distilled water (50 ml) followed by 2% HCl (50 ml). This mixture was extracted with ether (5 x 50 ml), after filtration through celite, and the ethereal extract washed with water, dried over anhydrous MgSO_4 and concentrated to a volume of 50 ml. GLC analysis of the reaction mixture by the calibration method yielded toluene (20%) and 4,4'-dimethylbiphenyl (2%). The reaction mixture was charged over a silica-gel column

and eluted with petroleum ether (b.p. 60-80°C) and benzene mixture (3:1, v/v), when di-p-tolylmercury (0.392 g; ca. 41%); m.p. 235°C; lit.⁵⁵ m.p. 236°C was obtained. Further elution of the column with a mixture of petroleum ether (b.p. 60-80°C) and benzene in the ratio 1:1 (v/v) yielded unreacted p-tolylmercuric chloride (0.425 g; ca. 26%) m.p. 238°C; lit.⁵² m.p. 238-239°C. The compounds were identified by GLC, mixed melting point technique and comparison of their IR spectra with those obtained for the authentic samples.

(b) Reaction of p-tolylmercuric chloride with LAH in molar ratio - 2:1; reaction time - 30 min

To a solution of p-tolylmercuric chloride (1.633 g; 0.005 mol) in dry THF (30 ml), kept under nitrogen atmosphere was added LAH (0.1 g; 0.0025 mol) contained in 30 ml of dry THF. Hydrogen gas (35 ml as at NTP) was evolved. Reaction mixture was worked up after 30 minutes. GLC analysis and column chromatography as described for the reaction 8(a), gave toluene (16%), 4,4'-dimethylbiphenyl (2%), di-p-tolylmercury (0.363 g; ca. 38%) and unreacted p-tolylmercuric chloride (0.506 g; ca. 31%).

(c) Reaction of p-tolylmercuric chloride with LAH in molar ratio - 4:1; reaction time - 30 min

Addition of LAH (0.05 g; 0.00125 mol) contained in dry THF (30 ml) to a solution of p-tolylmercuric chloride (1.633 g; 0.005 mol) in dry THF (30 ml) under nitrogen atmosphere at room temperature liberated 21 ml (as at NTP) of hydrogen gas. On work up

of the reaction mixture and subsequent GLC analysis and separation of the products by column chromatography, as detailed for the reaction 8(a), toluene (10%), 4,4'-dimethyldiphenyl (2%), di-p-tolylmercury (0.315 g; ca. 33%) and unreacted p-tolylmercuric chloride (0.653 g; ca. 40%) were obtained.

9. Reactions of p-nitrophenylmercuric chloride with lithium aluminium hydride (LAH) at room temperature under nitrogen atmosphere

(a) Reaction of p-nitrophenylmercuric chloride with LAH in molar ratio - 2:1; reaction time - 30 min

LAH (0.1 g; 0.0025 mol) contained in 30 ml of the dry THF was added to a solution of p-nitrophenylmercuric chloride (1.788 g; 0.005 mol) in dry THF (30 ml), under nitrogen atmosphere, when 51 ml (as at NTP, after accounting for the gas evolved in a control experiment under identical conditions) of hydrogen gas was evolved. Reaction mixture was worked up after 30 min by first adding distilled water and then 2% HCl. Ethereal extract of the reaction mixture was washed with water, dried over anhydrous MgSO_4 , filtered and concentrated to a volume of 50 ml. GLC analysis of this mixture using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length, by the calibration method yielded nitrobenzene (21%) and 4,4'-dinitrobiphenyl (3%). The reaction mixture was chromatographed on a silica-gel (100-200 M) column. Elution of the column with petroleum-ether (b.p. 60-80°C) yielded traces of azobenzene and azoxybenzene. Further elution of the column with a mixture of petroleum-ether (b.p. 60-80°C) and benzene in the

ratio 3:1 (v/v) yielded nitrobenzene (0.129 g; ca. 21%). Elution of the column with benzene yielded 4,4'-dinitrobiphenyl (0.018 g; ca. 3%). Further elution of the column with a mixture of chloroform and ethylacetate in the ratio 9:1 (v/v) yielded the unreacted p-nitrophenylmercuric chloride (0.089 g; ca. 5%); m.p. 263°C; lit.⁵² m.p. 265°C. Elution of the column with a mixture of chloroform and ethylacetate in the ratio 1:1 (v/v) yielded di-p-nitrophenylmercury (0.5 g; ca. 45%); m.p. 318°C; lit.⁵⁵ m.p. 320°C. Elution of the column with ethylacetate yielded a colored pasty mass, which could not be analyzed. The compounds were characterized by the mixed melting point technique, GLC, TLC, and comparison of their IR spectra with those of the authentic samples.

(b) Reaction of p-nitrophenylmercuric chloride with LAH in molar ratio - 4:1; reaction time - 30 min

To a solution of p-nitrophenylmercuric chloride (1.788 g; 0.005 mol) in dry THF (30 ml) kept at room temperature under nitrogen atmosphere, was added LAH (0.05 g; 0.00125 mol) contained in 30 ml of dry THF. Hydrogen gas (37 ml as at NTP) was evolved. Reaction mixture was worked up after 30 min in the usual manner. GLC analysis by the calibration method and column chromatography over activated silica-gel as detailed for the reaction 9(a), yielded nitrobenzene (10%), 4,4'-dinitrobiphenyl (3%), di-p-nitrophenylmercury (0.466 g; ca. 42%) and unreacted p-nitrophenylmercuric chloride (0.34 g; ca. 19%), besides traces of azobenzene and azoxybenzene.

10. Attempted control reaction of lithium aluminium hydride with cumene at room temperature under nitrogen atmosphere

LAH (0.19 g; 0.005 mol) contained in 30 ml of THF was added to a solution of cumene (0.6 g; 0.005 mol) in 30 ml of THF kept at room temperature (30°C) under nitrogen atmosphere. No hydrogen gas was evolved. The reaction mixture was worked up after 30 min in the usual manner. On extraction and isolation, unchanged starting hydrocarbon was recovered quantitatively.

11. Attempted control reaction of LAH with naphthalene at room temperature under nitrogen atmosphere

To a solution of naphthalene (0.64 g; 0.005 mol) in dry THF (30 ml) was added LAH (0.19 g; 0.005 mol) contained in 30 ml of dry THF under conditions identical to that employed for the reaction 7(e). No hydrogen gas was evolved. On working up the reaction mixture after 30 min. in the usual manner, the unchanged starting hydrocarbon was recovered quantitatively.

12. Reaction of dibenzylmercury with sodium naphthalene in equimolar amounts at room temperature (30°C) under nitrogen atmosphere; reaction time - 30 min

A solution of dibenzylmercury (1.91 g; 5×10^{-3} mol) in 30 ml of dry THF was placed in a 3-neck 250 ml RB flask. The contents of the flask were flushed with dry nitrogen for 30 min under magnetic stirring. Sodium naphthalene (5×10^{-3} mol) contained in 30 ml of dry THF was added through a pressure equalizing dropping funnel. The solution turned greenish-grey in color, due to

the precipitation of finely divided mercury. The reaction mixture was worked up in the usual manner, and qualitatively analyzed by GLC and TLC. The various products identified were toluene, bibenzyl and unreacted dibenzylmercury.

13. Reaction of dibenzylmercury with an equimolar amount of lithium aluminium hydride, at room temperature (30°C) under nitrogen atmosphere; reaction time - 30 min

In a 3-neck RB flask mounted over a magnetic stirring base, was placed a solution of dibenzylmercury (1.91 g; 5×10^{-3} mol) in 30 ml of dry THF. The solution was purged with dry nitrogen gas and lithium aluminium hydride (0.19 g; 5×10^{-3} mol) contained in dry THF (30 ml) was added through the dropping funnel. Hydrogen gas (53 ml as at NTP, after accounting for the gas evolved in a control experiment under identical reaction conditions) was evolved, with simultaneous precipitation of metallic mercury in a greenish-grey form. The reaction mixture on work up as usual was qualitatively analyzed by GLC and TLC. The products identified were toluene, bibenzyl and a small amount of unreacted dibenzylmercury.

V.5 References

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CHAPTER VI

SUMMARY AND CONCLUSION

In this thesis, reactions of six different categories have been examined in some detail and new mechanistic interpretations offered in each case. Various categories of reactions are:

(i) reactions of diaryliodonium cations with ambident 2-nitropropanate anion, in methanol solvent at room temperature (30°C) under nitrogen atmosphere,

(ii) radical nucleophilic substitution reaction of arene-diazonium cations with ambident nitrite anion, in methanol medium at 0°C under nitrogen atmosphere,

(iii) reactions of arenediazonium cations with ambident 2-nitropropanate anion in methanol solvent at 0°C under nitrogen atmosphere,

(iv) reactions of arenediazonium cations with benzylmagnesium chloride and tert.butylmagnesium chloride in THF medium at room temperature (30°C) under nitrogen atmosphere.

(v) sodium naphthalene induced reductive demercuration and symmetrization of organomercuric halides in THF medium at room temperature (30°C) under nitrogen atmosphere, and

(vi) reduction of organomercuric halides with lithium aluminium hydride in THF solvent at room temperature (30°C) under nitrogen atmosphere.

The reactions of diphenyliodonium bromide, phenyl-p-tolyl-iodonium bromide and phenyl-p-anisyl-iodonium bromide with lithium 2-nitropropan-2-ide yielded arylated nitroparaffins, monomeric hydrocarbons, dimeric products and formaldehyde in addition to iodoarenes. These reactions are catalyzed by light and inhibited in the presence of oxygen. In the presence of α -methylstyrene, the formation of arylated nitroparaffins is enhanced while the yields of monomeric aromatic hydrocarbons, biaryls and formaldehyde are repressed. This fact lends credence to the formation in these reactions, of arylated nitroparaffins on one hand and benzene, toluene, anisole, biaryls and formaldehyde on the other, by two competing pathways. The possibilities of occurrence of an S_NAr process and the intervention of aryne intermediates, in these reactions have been eliminated. Simultaneous occurrence of free radical cage and chain mechanisms initiated by single electron transfer from the 2-nitropropanate

anion to the diaryliodonium cation has been proposed to satisfactorily account for the observed experimental facts. The formation of arylated nitroparaffins occurs via a cage collapse mechanism, whereas benzene, toluene and anisole are produced by a radical chain mechanism. Here, the chain is propagated by the transfer of an electron from the hydroxymethyl radical $\cdot\text{CH}_2\text{OH}$ produced in the medium to the diaryliodonium cation. The departure aptitudes of p-methylphenyl and p-methoxyphenyl radicals from the diphenyliodine, formed in the solvent cage, are influenced by the presence of 2-nitropropyl radical in the cage.

The reactions of benzenediazonium fluoroborate, p-nitrobenzenediazonium fluoroborate and p-methoxybenzenediazonium fluoroborate with sodium nitrite yielded protodediazoniated products and nitroarenes besides biaryls, phenols and formaldehyde. Although the arenediazonium fluoroborates being studied are stable under our reaction conditions, the addition of sodium nitrite results in an instantaneous evolution of nitrogen gas. The reaction with p-nitrobenzenediazonium fluoroborate is faster and that with p-methoxybenzenediazonium fluoroborate slower compared to the reaction of benzenediazonium fluoroborate. These reactions are catalyzed by light as well as Cu(II) ions and inhibited by molecular oxygen. Intervention of radicals, in these reactions has been established and the possibility of formation of these intermediates via the thermolysis of covalent diazonitrites is ruled out. A free radical chain mechanism initiated by the transfer of an electron from the nitrite ion to the LUMO of

arenediazonium cation and proceeding via the formation of nitro-arene radical anion has been proposed to account for the observed facts.

The reactions of benzenediazonium fluoroborate, and p-methoxybenzenediazonium fluoroborate with lithium 2-nitropropan-2-ide yielded benzeneazo-2-(2-nitro)propane and p-methoxybenzeneazo-2-(2-nitro)propane, respectively. On the other hand, the reaction of p-nitrobenzenediazonium fluoroborate yields p-nitrobenzeneazo-2-(2-nitro)propane as well as the dediazoniated products. Occurrence of dediazonation via an S_NAr pathway or by the decomposition of the covalent azocoupling product is considered unlikely. It has been demonstrated that though the covalent azo compounds are produced by the ionic coupling, dediazonation occurs via parallel free radical chain mechanism. In the presence of Cu(I), even benzenediazonium fluoroborate and p-methoxybenzenediazonium fluoroborate partly react with lithium 2-nitropropan-2-ide by an electron transfer mechanism resulting in the formation of products accompanied by the evolution of nitrogen gas. This constitutes a new example of an entrainment process.

The reactions of five arenediazonium fluoroborates $p-R-C_6H_4-N^+ \equiv NBF_4^-$, namely benzenediazonium fluoroborate, p-nitrobenzenediazonium fluoroborate, p-methoxybenzenediazonium fluoroborate, p-acetylbenzenediazonium fluoroborate and p-methylbenzenediazonium fluoroborate with benzylmagnesium chloride as well as tert.butylmagnesium chloride, $R'-MgCl$, in equimolar ratios

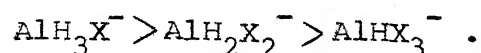
yielded dediazoniated products viz. $R-C_6H_5$, $p-R-C_6H_4-R'$, $R'-R'$, $R'-H$ and mixtures of isomeric biaryls (excepting with benzenediazonium cation, when diphenyl is the only biaryl formed). These reactions are inhibited by the presence of α -methylstyrene. Distinct ESR signals, absent in the pure reactants, were observed in the reaction of *p*-nitrobenzenediazonium fluoroborate with benzylmagnesium chloride. These and other observations have been rationalized in terms of the intermediacy of aryl and alkyl radicals, produced as a result of an electron transfer from the Grignard reagent $R'-MgCl$ to the π -system of the arenediazonium cation in an initially formed π -complex between the two reactants. It is found that only a minor component of the reaction may involve the formation of covalent azo compounds by an ionic pathway. It has been confirmed that the covalent azo compounds are not the precursors of radical intermediates.

The reactions of four organomercuric chlorides $R-Hg-Cl$ viz. benzylmercuric chloride, phenylmercuric chloride, *p*-tolylmercuric chloride, and *p*-nitrophenylmercuric chloride with sodium naphthalene gave diorganomercurials R_2Hg , monomeric hydrocarbons $R-H$, dimeric products $R-R$ and naphthalene in addition to metallic mercury. The conceivable formation of alkyl/aryl anions in the reactions with equimolar quantities of sodium naphthalene has been ruled out, since these species could not be trapped in separate control experiments. In the presence of cumene - a good hydrogen atom donor to radicals, reductive

demercuration leading to product R-H, predominates over symmetrization. Nucleophilic displacement of Cl^- by naphthalene radical anion on the electrophilic mercury of R-Hg-Cl is considered unlikely, in view of the observation that 9-fluorenyl anion, an equally good nucleophile vis a vis naphthalene radical anion, does not undergo such a substitution reaction. These reactions are retarded in the presence of added naphthalene from outside. As naphthalene radical anion is known to be an excellent electron donating species, a free radical mechanism initiated by a reversible $\pi^* \rightarrow \pi^*$ electron transfer from the naphthalene radical anion to the organomercuric halide has been proposed, to rationalize all the observations recorded for these reactions. Most reasonable process leading to the radical induced symmetrization of organomercuric chlorides, in the presence of an electron donor seems to be the reduction of an adduct $[\text{R}_2\text{HgCl}]^\bullet$, formed by the addition of radical R^\bullet to RHgCl . The observed increase in the yields of monomeric hydrocarbons R-H, in the reactions employing twice the molar amount of sodium naphthalene is in agreement with the proposed formation of alkyl or aryl anions from the corresponding radicals, in the presence of an excess of naphthalene radical anion. Initial results have indicated that a similar electron transfer free radical mechanism is operative in the reduction of diorganomercurials with naphthalene radical anion.

Reduction of the same organomercuric chlorides R-Hg-Cl as mentioned above, with lithium aluminium hydride yields diorganomercurials, monomeric hydrocarbons R-H, dimeric products R-R and

anion AlH_3^- , which in turn, transfers its extra electron to the organomercuric halide, in competition with AlH_4^- . Mixed hydrides AlH_3X^- , AlH_2X_2^- and AlHX_3^- when produced in the medium, serve the same purposes as inferior alternatives to AlH_4^- , with the efficiency decreasing in the order:



Studies reported in this thesis have thus led to some new mechanisms involving electron transfer in the reactions of diaryliodonium and arenediazonium cations as well as organomercuric halides with ambident anions, aromatic radical anions and metal hydrides. Besides their mechanistic significance, these electron transfer reactions may conceivably provide convenient, mild condition routes to otherwise cumbersome chemical transformations.

VITAE

Born on 28th October, 1954 at Meerut, Rajive Kumar Khanna passed his Indian School Certificate Examination from St. Mary's Academy, Meerut, in 1971. Later, he joined St. Stephen's College, Delhi and received the degree of Bachelor of Science in Chemistry (Hons.) from the University of Delhi in 1974. He obtained the degree of Master of Science from Indian Institute of Technology, Delhi, in 1976 and joined the graduate programme in the Department of Chemistry, Indian Institute of Technology, Kanpur in July 1976. Presently, he is a Research Assistant in the Department of Chemistry.